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THIS MONTH'S COVER

• *B. E. Morrow Steam Plant of Consumers Power Company, located near Kalamazoo, Mich. It contains two 35,000 kw generators and one 50,000 kw generator, with an additional 60,000 kw unit under construction. Steam pressure is 850 pounds at 900° F. Like all power utilities, Consumers Power has encountered many corrosion problems in plant as well as in the distribution system. A comprehensive article on transmission corrosion problems starts on page 133.*

IT ISN'T RAINING VIOLETS ... BUT

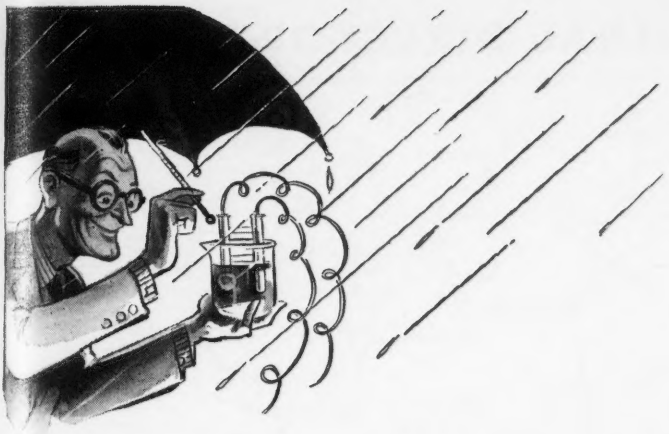
"EACH RAINDROP makes some flowerlet blow," sings the poet. With his inward eye he can even see violets in a January rainstorm. But the corrosion engineer is just mean enough to collect some of that rain water and measure the pH of it.

British scientists studying atmospheric pollution have found that in the Battersea Park area of London, the pH of rain is 3.9 in January and 5.0 in July. That is, the hydrogen ion concentration varies from 0.00013 normal in winter to 0.00001 in summer. In the main this is due to sulfuric acid derived from sulfur oxides thrown into the air by the burning of industrial and domestic fuels. In some industrial towns, the pH of rain is below 3.0 at all seasons, which is to say the acidity is greater than 0.001 normal. And some towns even have measurable amounts of ammonia in their rain supply.

MORE TRUTH AND LESS POETRY IN CORROSION DATA

These facts are of interest when one considers the general problem of atmospheric corrosion. In view of the varying conditions that exist from one locality to another, one must use the utmost caution in taking data derived from laboratory tests

Atmospheric corrosion test specimens exposed to a marine atmosphere at Kure Beach, N. C. Similar exposures are made by INCO *in an industrial area at Bayonne, N. J., and in a rural district. Below can be seen the manner of mounting specimens between insulators.*



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and applying them to atmospheric uses; and in relying on data from one outdoor test location to estimate behavior in a different atmospheric environment somewhere else.

Laboratory exposure data are not necessarily consistent with the results obtained from atmospheric performance. In addition to seasonal changes, which involve temperature variations, the amount of rainfall, the kind of local pollution and the extent of it, and the length of time the surfaces remain wet must be considered. Protective measures must obviously be based on data derived under natural conditions. Even data derived in this way must be properly interpreted to account for differences between the behavior of specimens at rest and of fabricated equipment subject to the usual strains, vibrations, abrasion, and so on.

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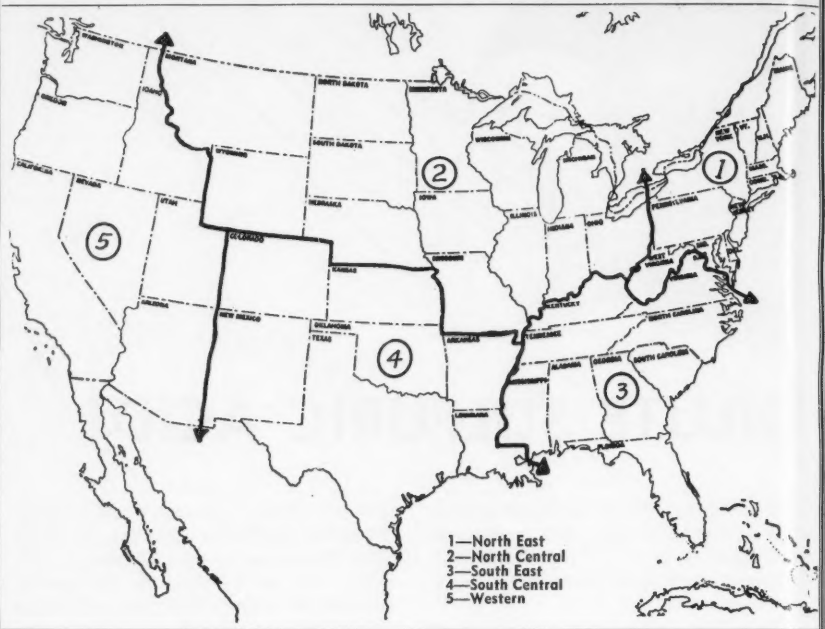

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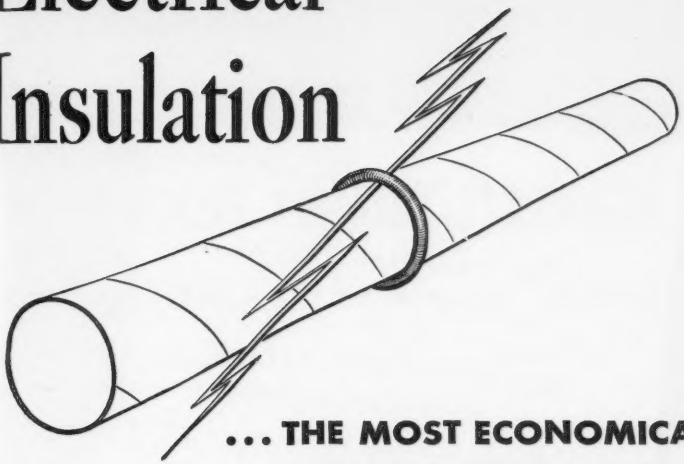

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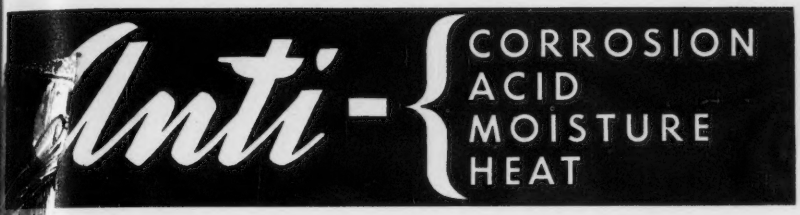

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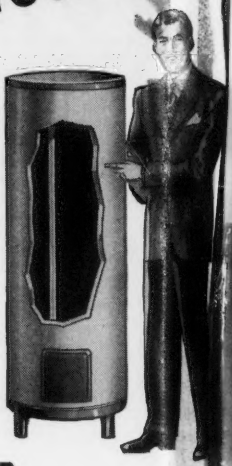

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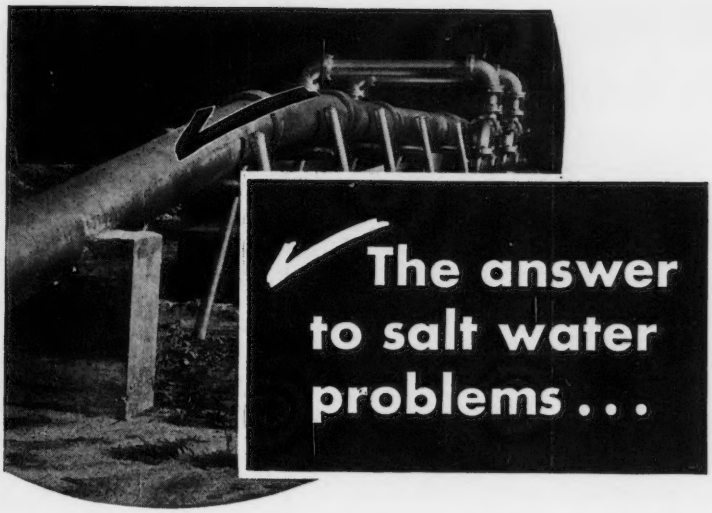

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(a) to promote scientific research in determining the causes of corrosion and methods of its control with respect to theory and practice.

(b) to provide a means of exchange of knowledge and ideas among those individuals actively engaged in the control of corrosion.

(c) to promote methods of control of corrosion.

(d) to promote standardization of terminology, methods, equipment and design in the development of methods of corrosion control.

(e) to foster cooperation between individaul owners of metallic structures in the solution of their joint corrosion problems.

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Effect of Atmospheric Corrosion on Maintenance and Economics of Overhead Line Hardware and Guy Strand*—Part 1

By C. J. Couy*

THIS article is an abstract of the first part of an engineering study for the rationalization of the maintenance of a large electric distribution system, by the investigation of the aging or "wearing" characteristics of the component materials and the application to the task of information so secured.

The study is approached from the operating engineer's point of view in that it is attempted to coordinate an extremely variable mass of data and arrive at rational results useful in the maintenance of the system up to the standards of safety imposed by governmental regulations or minimum engineering requirements, and accomplish this with as little waste as possible.

No attempt is herein made to discuss corrosion theory and, beyond a simple statement of the characteristic atmospheric corrosion forms of the most common construction metals, the following discussion is based as much as possible on data from local experience in the Pittsburgh district and on published data applicable to that or similar industrial areas.

A method of application of such data to system maintenance and to the economic selection of new or substitute material is presented.

Scope

The problem of the economical operation of any structure or system of structural units, posed by the deterioration with age of its component materials or parts, devolves basically into the following three phases:

1. Determination of the correct time for replacements.
2. Development of an organization and a program for the routine effectuation of the requisite replacements.
3. Use of available technical information and data to the application of deterioration retarding measures and the selection of such new parts and materials for use in the replacements as will result in more economical future operation, as measured by lowered annual costs.

★A paper presented at the Annual Meeting of NACE in Chicago, Ill., April 7-10, 1947.
* Duquesne Light Co., Pittsburgh, Pa.

This article is concerned with the first and third phases of the problem as it specifically applies to overhead electric line hardware.

Deterioration of Overhead Line Hardware in Industrial Exposure

Service Life

The service life of any structure, metallic or of any other material is determined by its rate of aging or decay:

where

$$L = \frac{1 - P}{R} + C \qquad [1]$$

L = service life, years.
P = minimum permissible parameter, fraction of original.
R = annual rate of decay of parameter, fraction of original.
C = coating effectiveness, year.

Similarly, the remaining life of the structure, L′, would be

$$L' = \frac{P' - P}{R} \qquad [2]$$

where P′ is the parameter, expressed as a fraction of original, at the time of the investigation.

Thus, a knowledge of decay or corrosion rates would seem to be indispensable in the intelligent design and maintenance of structures of any sort.

Atmospheric Corrosion Characteristics of Common Structural Metals

It is known that the atmospheric corrosion rates of various metals, in similar atmospheric exposure, are very different from each other and depend on the type of surface film formed by the corrosion product on the metal surface. In Figure 1 are

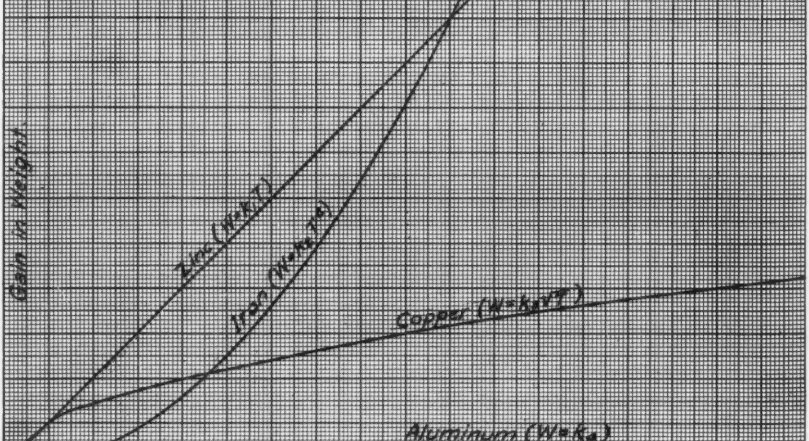

Figure 1—General corrosion rate forms.

presented typical corrosion product weight-time relationships resulting from exposure in dry, indoor, urban atmosphere of the four metals most used in the electric central station industry.[1] These graphs are not to scale, being merely intended to indicate the characteristic form of the process.

It will be noted that for aluminum the weight-time relationship rises sharply to a constant value, indicating an adherent, continuous, impervious and self-healing corrosion product surface film. Incidentally, this is also very nearly the characteristic for lead.

This relationship for copper assumes a parabolic form, indicating the process to be controlled by the diffusion of the corrodent through an increasingly thick and inert surface film.

The characteristic for zinc is linear, indicating a constant rate of attack because of a porous or granular non-protective film.

Finally, the inverted parabolic relation shown for iron indicates the accelerating effect of the hygroscopic as well as discontinuous corrosion film.

The metal corrosion characteristics of Figure 1 apply to exposure in dry, indoor, urban atmosphere and would be entirely different for exposure in a different environment, e.g., ammonia fumes. For an exposure to outdoor, urban, or industrial atmosphere, in which the most active and abundant corrodent by far is sulfur dioxide, these metals would exhibit the respective corrosion-time characteristic forms about as shown in Figure 1.

From this it is seen that aluminum, copper and lead* are practically immune to ordinary urban or industrial atmospheric attack, while iron and zinc are constantly attacked. This is the dissolution tendency characteristic of the metal.

The final rate of atmospheric attack of a reactive metal is primarily defined by the combination of the factors of: (1) metal dissolution tendency as indicated in Figure 1; (2) proportion of total time moisture is present; (3) the amount of severity of atmospheric pollution. This last, in solution in the moisture film on the metal surface constitutes the electrolyte of an electrochemical dissolution cell. The presence of abundant dissolved atmospheric oxygen makes the cell very active.

The above combination of variable primary factors plus the additional effect of such other variables as metallic impurities, electrolyte and corrosion product migration, etc., result in the almost baffling effects observed in practice.

Atmospheric Corrosion Rates

A detailed discussion of corrosion rates is out of place here, a wealth of material being available elsewhere. The discussion that follows is confined to a statement of the upper and lower limits of rates and the effect of these on the service life of the material in the urban industrial area of Pittsburgh.

Ferrous Atmospheric Corrosion

The rates of atmospheric attack for the ferrous group are the most variable of those for any of the structural metals, the reason being

* Lead is not shown on graph, but would be practically parallel with aluminum.

TABLE I

Relative Corrosion of Ferrous Metals in Industrial Atmosphere, Pittsburgh, Pennsylvania

Type Designation	AVERAGE ANALYSIS, PERCENT						Average Life, Months	Average Penetration Inch per Year*
	Carbon	Manganese	Phosphorus	Sulfur	Silicon	Copper		
Copper Bessemer Steel	0.041 0.06	0.366 0.287	0.096 0.030	0.062 0.051	0.008 0.006	0.277 0.277	73.7+[a]	0.00255—
Copper Acid Open-Hearth Steel	0.107 0.107	0.447 0.447	0.091 0.091	0.046 0.046	0.004 0.004	0.237 0.237	69.3+[b]	0.00271—
Copper Basic Open-Hearth Steel	0.076 0.079	0.358 0.369	0.019 0.017	0.037 0.033	0.007 0.007	0.235 0.230	50.4	0.00372
Copper Pure Iron	0.017 0.017	0.054 0.053	0.007 0.007	0.031 0.031	0.005 0.004	0.260 0.259	43.8	0.00428
Copper Wrought Iron	0.033 0.033	0.034 0.034	0.114 0.114	0.021 0.021	0.134 0.134	0.283 0.283	31.5	0.00595
Low-Copper Wrought Iron	0.03 0.03	0.055 0.055	0.139 0.139	0.021 0.021	0.218 0.218	0.020 0.020	28.0	0.00669 (1.125)
Low-Copper Pure Iron	0.02 0.02	0.036 0.037	0.006 0.006	0.025 0.026	0.004 0.004	0.024 0.024	22.8	0.00822 (1.92)
Low-Copper Basic Open-Hearth Steel	0.117 0.112	0.493 0.505	0.020 0.016	0.033 0.032	0.199 0.214	0.020 0.020	17.2	0.01090 (2.93)
Low-Copper Bessemer Steel	0.041 0.042	0.384 0.392	0.094 0.091	0.046 0.041	0.006 0.007	0.014 0.014	16.9	0.01110 (4.35)

Summary of data published by the American Society for Testing Materials on 22-gage, uncoated sheets of various types exposed on racks to the atmosphere of Pittsburgh, Pennsylvania, for 75 months. Based on the average of the sheets of each class. Copper bearing material contains 0.15 percent Cu or over, and non-copper material 0.03 percent Cu or less. Failure means penetration of the sheet.

[a] Eighteen of the 23 sheets exposed had not failed at the end of the test.

[b] Five of the 16 sheets exposed had not failed at the end of the test.

Sheets that had not failed were given a life of 75 or 132 months (when the test was discontinued) for calculating purposes. They were in excellent condition.

* Numbers in parenthesis are the ratio of the penetration rate for the low-copper to that for the corresponding copper-bearing metal.

the variability of composition, resulting in an almost unlimited combination of all physical characteristics, corrosion tendency being one.

Generally, malleable iron and cast iron seem more resistant to attack than mild steel, because of the more finely grained and adherent coating of rust formed on them. Wrought iron and steel exhibit variables susceptibility to attack, neither being consistently better than the other. The inclusion of 0.15 percent to 0.25 percent copper in steel markedly improves its resistance to atmospheric corrosion.

Table I is a summary of ASTM tests of 22-gage uncoated ferrous sheets of various composition exposed in Pittsburgh atmosphere, arranged in descending order of corrosion resistance.[2] The range varies between 2.5 and 11 mills penetration per year, the lower half of this range being taken up by the copper bearing sheets.

Table II has been computed to show the probable service life of low-copper and of copper-bearing sheet steel in severe Pittsburgh area, on the basis of the penetration rates of Table I and on the assumption of a total permissible loss of 100 percent of the original thickness. From this it appears that the ultimate service life in Pittsburgh of line

hardware parts made of 6-, 7-, 9- and 11-gage sheet is only six to ten years after the disappearance of the zinc coating. Line hardware made in whole or in part of such sheet include some of the lighter low voltage insulator pins, secondary racks, thimble clevises, pin-straps, various of the smaller clevises, etc.

This would indicate that the corrosion resistance of the material rather than the strength rating of the unit when new should be the limiting design consideration for the lighter line hardware for use in industrial exposure.

It is also shown in Table II that the maximum increase in life possible by the use of copper-bearing steel for this class of material ranges between 19 and 30 years, which means a better than four times life-span, and makes its service life comparable to that of treated poles.

Use of the recently developed low-alloy steels, said to perform considerably better than copper-bearing steel in severe industrial exposure, would also warrant consideration for use on the lighter line hardware, based on first cost consideration. This will be discussed later.

While no quantitative data is at hand on the annual penetration rates of malleable iron used in the heavier units, such as strain and suspension clamps, strain insulator caps, etc., the experience in Pittsburgh has been a satisfactorily long life comparable to that of similar pieces made of forged copper-bearing steel. The lower corrosion rates on malleable iron and copper-steel, due to the finely grained and adherent rust coating formed, together with the larger sections employed on such units, account for the satisfactory performance.

TABLE II

Ultimate Service Life of Sheet Steel in Pittsburgh Area

(Based on Penetration of the Metal)

Annual penetration:—
Low-Copper Steel = 0.0110 inches
Copper Steel = 0.0025 inches

Gage No.	THICKNESS		SERVICE LIFE, YEARS	
	Inches	Decimal	Low-Copper Steel	Copper-Bearing Steel
22	1/32	0.03125	1.4	6.2
16	1/16	0.0625	2.8	12.5
11	1/8	0.125	5.7	25.0
9	5/32	0.156	7.1	31.2
7	3/16	0.1875	8.5	37.5
6	13/64	0.203	9.2	40.6
3	1/4	0.250	11.4	50.0

Generally, the service life of structural units of ferrous metal in atmospheric exposure is limited by local attack in certain parts of the unit, the rest being relatively intact. Ferrous metal is particularly subject to this type of failure.

Metallic Coatings

Because of their susceptibility to attack in urban and industrial atmosphere, ferrous metals, otherwise most suitable for structural work by reason of their physical characteristics and low cost, must be given protective coatings of paint or metal to economically increase their structural value. Paint being unsuitable to our purposes, only metallic coatings are considered.

Metallic coatings for outdoor steel are, or may be, made of one of four metals; zinc, copper, lead and aluminum.

Zinc is the most common outdoor metallic coating and has been longest so used. It is the coating now found on practically all line hard-

TABLE III

Condition of Galvanizing on Overhead Line Hardware As Affected by Aging in Vicinity of Pittsburgh, Pennsylvania

Type of Exposure	YEARS SINCE INSTALLATION											
	3	4	5	6	7	8	9	10	11	12	13	14
3/8" and 5/16" Guy Strand; 0.8 Oz./Sq. Ft. Coating Class												
Industrial	G	GY	70R	100R	100R–	G	100R	100R	100R	100R	100R	100R
	3	2	2	1	3	1	5	2	1	2	2	2
Urban	Y	G	GY	G	100R	100R	100R–		100R	100R	100R	100R
	1	2	2	2	2	2	2		2	2	1	2
Rural (Suburban)	G	G	G	G	G	Y	90R	10R	100R	100R	100R	
	2	2	2	2	2	2	2	1	2	1	2	
Bolts; 1.25 Oz./Sq. Ft. Coating Class												
Industrial	G	GY	Y	Y	Y	25R	100R	100R	100R–	100R	100R	100R
	4	4	4	7	9	9	4	6	8	8	10	4
Urban	G	G	G	GY	Y	50R	GY	100R	100R	100R–	100R–	100R
	4	4	5	4	4	2	4	2	2	2	4	4
Rural (Surburban)	G	G	G	G	G	Y	Y	50R	GY	GY	100R	GY
	8	4	4	4	4	4	4	4	4	4	5	2
Cross-Arm Braces; 2.0 Oz./Sq. Ft. Coating Class												
Industrial	G	G	G	GY	Y	GY	60R	90R	100R	100R	100R	75R
	3	6	3	2	3	6	8	3	2	5	2	5
Urban	G	G		G	GY	Y		75R	75R	10R	45R	100R
	3	2		2	2	1		2	2	2	3	5
Rural (Suburban)	G	G	G	G	G	G	GY	50R	GY	25R	50R	G
	2	2	3	3	2	3	2	2	3	2	4	1
Insulator Steel Pins; 2.0 Oz./Sq. Ft. Coating Class												
Industrial	G	G	G	GY	GY	GY	70R	90R	100R	75R	50R	75R
	8	12	2	4	9	8	10	2	11	6	8	4
Urban	G			G	25R	75R	GY	Y	75R	100R–	90R	100R
	4			4	5	4	2	4	4	6	10	8
Rural	G	G	G	G	G	GY	GY	GY	GY	10R	50R	G
	4	6	6	8	4	6	4	4	6	8	6	2
Secondary Wire Racks; 2.0 Oz./Sq. Ft. Coating Class												
Industrial	G	G	G	75R	GY	GY	50R	Y	50R	75R	60R	50R
	1	2	1	2	2	3	1	1	3	1	4	2
Urban	G	G	G	GY	GY	GY	GY		GY	25R	50R	50R
	1	1	2	3	2	1	3		1	2	1	3
Rural	G	G	G	G	G	G	GY	25R	GY	35R	GY	GY
	1	2	1	2	2	1	2	2	3	3	1	1

Symbols Used Above:

G=Gray GY=Rust Stained Gray R=Rust (preceded by percentage of rust-covered area) Y=Rust Stained.
Numerals below symbols indicate the number of units inspected.

ware, with the exception of copper-covered guy strand and some incidental items manufactured from copper-covered steel wire or rod, e.g., ground-rods staples, aerial cable rings, etc.

The extensive use of zinc as a coating for outdoor ferrous metal is attributable to its relatively low cost; its ease of application to iron with which it forms an alloy bond; its very satisfactory ductility when properly applied; and the fact that, being anodic to iron, protects it by immolation at any discontinuities or cracks that might develop. The most serious defect of zinc as a coating metal is its quite low corrosion resistance in both industrial and marine exposure, its corrosion

product in both acid or alkaline attack being non protective because it is porous and water-soluble.

The subject of atmospheric corrosion rates of zinc, because of its great economic importance, has received considerable study in all industrial countries and a great volume of information and data is available, applicable, as is the case with all such data, to the locale and conditions under which they were obtained, or to comparable ones.

Comprehensive exposure tests of zinc-coated material, in all types of atmosphere, have been made by American Society for Testing Materials, and the resulting reports contain extremely valuable information.

In an attempt to determine the progressive development of rust on the zinc-coated equipment under actual service exposure on our overhead system, an inspection of representative units of known installation dates ranging between 1930 and 1941, inclusive, was made at 72 locations, one-third each industrial, urban-residential and rural.

Units installed during every year of the twelve year period were inspected at two locations in each of the three kinds of exposure, six for each year of the twelve-year period covered. As many units of the types chosen as were available at each site were examined, the total number covered in the inspection being approximately 600.

As was to be expected, the condition of the individual units of equal age and apparently similar exposure varied, at times quite widely, evidently because of variations in the following: (a) shielding of certain units or parts of the same unit from complete exposure; (b) the severity of pollution at the locations chosen, which doubtless varied within each class, even the proper classification of certain sites being quite debatable; (c) the size, shape, and position in service of units of the same coating thickness class; (d) the thickness of coating on similar units.

TABLE IV

Average Atmospheric Corrosion Rates of Zinc Coatings on Overhead Line Hardware at Pittsburgh, Pennsylvania

ZINC COATING		AVERAGE ANNUAL PENETRATION, IN. x 10^{-4}		
Weight in Oz./Sq. Ft. of Surface	Thickness In. x 10^{-3}	Industrial	Urban Residential	Rural (Suburban)
0.80	1.36	2.26	1.94	1.70
1.25	2.13	2.37	2.13	1.78
2.00	3.40	2.83	2.61	2.26*

* Pessimistic.

Results of this inspection, given in Table III, were arrived at by first averaging the results for all the units of each kind at each site, then averaging the two resulting averages of similar exposure for each year. Results are as consistent as could be expected, and they indicate zinc coating life-expectancies in Pittsburgh, exposure of five to eight years for the 0.8-ounce, eight to 12 years for the 1.25-ounce, and ten to fourteen or more years for the 2.0-ounce coatings.

Results, converted into inch-per-year penetration are also presented in Table IV for comparison with other published data.

The durability of the zinc coating, as usually given, is the time required for its complete disappearance. There is some evidence that the effectiveness of the coating, as measured by the difference in the

length of the service life of a coated unit over that of an uncoated unit, is longer by two or three years than the durability. This is probably due to the protective effect of remaining traces of the bonding zinc-iron alloy. This would seem to apply particularly to the thinner coatings. On the heaviest coatings any non-uniformity or damage to the coating might result in exposing the iron to damaging attack long before the disappearance of the coating, this, incidentally, being one of the most serious disadvantages of very heavy zinc coatings.

While there has been considerable discussion and investigation of the comparative durability of the hot-dip and electrodeposition methods of coating guy strand, prevalent opinion is that the performance of equivalent coatings is equal.

Copper, if properly applied, results in a material of indefinitely long life because of its extremely low rate of atmospheric attack. Its serious disadvantages are a relatively high first cost and the fact that, being cathodic to steel it intensifies the attack on it at any imperfections in the coating and also where it comes in contact with steel or zinc, as at clamps and fixtures. Properly prepared and installed copper-coated units should be very durable and are particularly applicable to the severest industrial exposures.

Lead coatings, while difficult to apply to steel by hot-dipping because lead can form no bonding alloy with it, are otherwise very satisfactory, being pliable and inert in marine as well as industrial atmosphere. Unfortunately they are not in commercial production.

Aluminum coatings, also difficult to apply by hot-dipping, and brittle if too thickly applied, are very durable in industrial exposure. They are not in commercial production.

Lead and aluminum coatings on line hardware, if economically produced, would eventually result in far more long-range system maintenance programs, as well as lighter original designs. The industry should, therefore, take a much more leading role in the advocacy for their commercial production.

References

1. W. H. J. Vernon, Trans, Faraday Soc. **23**, 113 (1927).

2. F. N. Speller, Corrosion Causes and Prevention, (book) McGraw-Hill, New York, N. Y.

EDITOR'S NOTE: Part II of this three-part article will be reproduced in the May edition of CORROSION.

Chemical Research and Corrosion Control: Some Recent Contributions of a Corrosion Research Group *

*By W. H. J. Vernon**

Condensation by Ivy M. Parker**

THE prosecution of research on the corrosion of metals was one of the earliest activities of the Department of Scientific and Industrial Research, by whom a Corrosion Research Committee was set up in 1924 with the late G. D. Bengough as its senior investigator until 1936. This survey, the first since the war, covers the period from 1939[1] to date. Most of the work has been concerned with specific war-time problems.

High-Speed Rotor Apparatus

The High-Speed Rotor Apparatus[2] is based on researches carried out in the Section prior to the period under review; it was originally designed to investigate the corrosion resistance of unpainted metals to fresh waters or sea water under conditions of rapid movement. Each unit carries six specimens; these are mounted in a circular ebonite holder, which is itself carried by an ebonite-covered steel spindle, driven by a one-half horsepower electric motor. The spindle is inclined to the vertical, in order to avoid an undesirable vortex effect in the rectangular glass tank in which the liquid is contained. The specimens are small (one inch square), but when mounted flush in the holder their surfaces form virtually part of the rotating surface; they are normally insulated from each other, but can, if desired, be interconnected within the holder. This is normally rotated at a speed of 1500 rpm, giving a peripheral speed (checked by a simple stroboscopic device) of approximately 20 knots.

Using unprotected metal surfaces, the influence of various cations and anions on the rate of corrosion, both in sea water and in fresh waters, has been investigated in relation to speed of movement. (It has been shown, for example, that under moving conditions, sea water is appreciably less corrosive than an equivalent concentration of sodium chloride.) The influence of surface finish on corrosion rate is also being investigated.

The ability of the rotor apparatus to discriminate between good and bad compositions was put to use during the war, on behalf of Admiralty (DSRE), for the evaluation of a very large number of various coatings.

These were not necessarily ships bottom compositions; many other vital parts of a ship's structure and equipment make contact with rapidly moving and highly aerated sea

★ Chairman's Address to the London Section of the Society of Chemical Industry, October 7, 1946. Jour. Soc. Chem. Ind. **66**, 137-142 (1947) May.

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** Plantation Pipe Line Co., Atlanta, Ga.

water, for example, propellor shafts and various parts of the condenser systems. Accordingly, information was required on the most efficient methods of protecting such structures under the generally higher rates of working imposed by war conditions. It became necessary to develop, with the utmost speed, new paints showing improved adhesion to metal and greater resistance to deterioration in sea water, and for this reason a rapid method of appraisal was essential. A battery of 12 (later increased to 18) rotor units was in constant use, day and night, during the war, for this work. Coatings showing unsatisfactory adhesion to the underlying metal were rejected after test-periods of a few days—in extreme cases, after one day—thus avoiding waste of time in testing unsatisfactory materials. It was possible to indicate to paint manufacturers which types of paint showed most promise and hence to avoid delay in further development of the most suitable compositions. This resulted in a steady improvement in the protective properties of available paints. At the start of the investigation it was exceptional for a paint to survive a period of 50 days in the rotor test, but eventually a few compositions were developed which showed useful lives of several times that period. Ships' trials conducted by Admiralty have confirmed the conclusions drawn from tests carried out with the rotor apparatus.

The "sacrificial" use of zinc blocks for protecting the hulls of ships (originally* the copper sheathing of wooden vessels) has been continued for many years more or less empirically, and it is now realized that further work is needed. Our own experiments have been carried out partly with the rotor apparatus and partly in larger tanks permitting relatively long distances between anodes and cathodes, the sea water being kept well agitated by means of stirrers. Systematic measurements were made of anode and cathode potentials and of the current passing through the system; a preliminary investigation was also made of the conditions under which a steel anode connected to an external source of electromotive force can be substituted for a zinc anode.

So far we have considered corrosion control either by the purely exclusion method, as by high-duty coatings, or by modification of the corrosion mechanism itself, as in cathodic protection. A third method, which again involves control by way of the corrosion mechanism, concerns the use of small concentrations of corrosion inhibitors. Obviously, this is not possible in exposure to the open sea; but it does become possible in closed systems, as, for example, the water or solutions used in engine-cooling systems. This brings us to the subject of antifreeze solutions, which was a major charge on the time of the Section during several years of the war.

Antifreeze Solutions

The work on antifreeze solutions (carried out on behalf of Ministry of Supply) arose from the war-time need for substitutes for ethylene glycol or glycerine in automobile engine-cooling systems. The pre-

* On the suggestion of Sir Humphry Davy, following his experiments in describing which (Phil. Trans. **1824**, 242; **1825**, 328) he acknowledged "the assistance of Mr. Faraday."

requisites were? (1) Adequate freezing point depression in aqueous solution; (2) Satisfactory behavior at running temperatures (freedom from frothing, scale removal, etc.); (3) Absence of undue corrosion of any metal or combination of metals entering into the cooling system; (4) Availability under war-time conditions.

It is hardly necessary to refer to the typical eutectic freezing point curve that is the basis of antifreeze solutions. With some inorganic salts, notably calcium chloride, the eutectic temperature is extremely low and such salts have high antifreeze efficiency; on the other hand, they are commonly highly corrosive in aqueous solution. Organic depressants, such as glycol and glycerine combine thermal efficiency with considerably less corrosive action towards metals in radiator systems. The problem, therefore, was either to find an entirely new antifrigerant that would satisfy the requirements stated, or alternatively, to find sufficiently satisfactory corrosion inhibitors to permit the use of inorganic salts in common supply.

The outstanding finding of the antifreeze work relates to sodium benzoate, the valuable properties of which in this connection appear hitherto to have escaped attention.* Not only is sodium benzoate a fairly efficient antifrigerant (e.g., 30 percent solution with freezing point of —10° C.), but in antifreeze concentrations it is practically non-corrosive towards iron and steel and other metals commonly used in radiator systems, even under the drastic conditions of circulation and intermittent heating and cooling.[3]

Sodium benzoate falls into the category of a "safe inhibitor," since if insufficient quantity is added to afford complete inhibition there is no tendency to localized attack and the position is at least no worse than if the inhibitor were not present. Electrode potential measurements have shown that sodium benzoate functions as an anodic inhibitor, but the precise mechanism is not yet clear. A film has been stripped from benzoate-treated steel, using the technique previously described.[4] Other promising organic inhibitors are now being investigated.

As opposed to contact with the liquid in bulk, as in the cases hitherto considered, in the de-icing and de-frosting systems of aircraft, the metal is exposed to no more than a film or thin layer of the corroding liquid. Under such conditions the controlling factors are different from those of complete immersion, and we have here, in fact, an essentially different problem. Technically, its importance arises from the fact that a relatively small amount of corrosion can interfere with the efficient working of the system.

In cooperation with Royal Aircraft Establishment, Farnborough, an investigation was carried out with a view to finding inhibitors that would prevent the troubles from corrosion that had, in fact, been experienced in service. The de-icing fluid preferred at that time contained ethylene glycol and industrial methylated spirit, with 10 percent water. The metals with which this mixture came in contact included, besides

* In respect, however, to corrosion inhibition, J. M. Bryan, in the course of experiments with pure aluminum in solutions of sodium salts of organic acids at 25° C., observed the absence of corrosion in solutions of sodium benzoate.

duralumin and aluminum, ordinary and stainless steel, copper and brass, and tinman's solder. Corrosion occurred principally on the solder which was used for the "wick feed" conveying the liquid to the aeroplane wings; most of it probably occurred at ordinary temperatures when the system was not in operation—although charged, of course, with the liquid.

The technique employed in the tests provided for the exposure of specimens and composite specimens to thin layers of the fluid; special attention was given to soldered surfaces and a method was devised for the rapid soldering of specimens under reproducible conditions. Some 200 substances were examined for possible inhibitive properties; the criteria adopted in the final selection were freedom from corrosion on the metal on the one hand, and, on the other hand, clearness of the liquid (absence of suspended or precipitated matter at the conclusion of the test) both at ordinary temperatures and at temperatures down to —40° C. On this basis, the choice reduced to a short list of six inhibitors, shown in Table I (in order of efficiency).[5]

TABLE I

INHIBITOR	Percent†
Sodium selenate	0.2
Sodium arsenate	0.5
Sodium salt of fluorescein	0.5
Potassium chromate	1.0
Sodium cinnamate	1.0
Sodium selenite	1.0

† Gallons per 100 ml. of de-icing fluid.

Steel specimens wrapped in paper, treated simply by dipping in a five percent aqueous solution of sodium benzoate and drying off, have remained completely bright after prolonged exposure in a warm humid atmosphere (intermittently precipitating moisture) in which specimens wrapped in untreated paper have rusted severely. The work has been extended to cover cellulosic materials in general and impregnating agents of similar type, including various esters of benzoic and related organic media.[6]

A problem closely alied to the one just discussed is that of preventing corrosion of metals in an enclosed space of air, as in packages or containers, by means of volatile inhibitors. The object here is to avoid the need for actual contact with the wrapping material and to rely upon the presence of the inhibitor in the vapor phase.

For this investigation, a wide range of materials has been examined, using a technique in which air, almost saturated with water vapor at 35° C., is slowly led through glass vessels (also at 35° C.) in which are contained selected metal specimens together with the reagent under test. In view of the successful results obtained from benzoates in the other packaging work, volatile benzoates, with volatile esters of other aromatic acids, were included in the tests. The general outcome of the work has been very encouraging, the most successful results so far having been obtained from the use of *n*-butyl benzoate.[7] For steel and aluminum, the quantity of ester required is very small since it merely needs to be enough to saturate the atmosphere of the package with the vapor of the inhibitor. The esters are insoluble in water, so there is little tendency for leaching out should the wrapping material become saturated with water.

This subject of corrosion in en-

closed spaces obviously falls into the category of atmospheric corrosion, and it has not been possible—during the war or immediately after—to pursue the more fundamental investigations in this field that were in progress in the Section up to 1939.[8] Some of the findings of this work, particularly in respect to critical humidity phenomena, found application during the war in connection with corrosion problems in the jungle. There, it is the rule rather than the exception to have to deal with relative humidities exceding critical values found in laboratory work; but there is at least the satisfaction of knowing that it is only necessary to reduce the humidity below the critical value—which after all is fairly high—to enter the region of safety, and any attempt to reach lower values is, from the corrosion point of view, so much effort wasted. Work[4] on quantitative examination of surface oxide films has been resumed.

Accelerated Atmospheric Corrosion Tests

In 1939, the possibilities of an apparatus were being examined. The original form of this apparatus was due to Schroeder, as developed by Swinden and Stevenson,[9] to whom we were indebted for a prototype. In this scheme, the specimens are carried on an endless motor-driven belt and, in the course of their slow rotation, sprayed with appproppriate solutions, with alternate drying.

Modifications made at Teddington have been in two main directions. First, seeking to incorporate the finding of the long-range researches on atmospheric corrosion, particularly in respect to the fundamental part played by disperse solid particles in the atmosphere and by traces of sulfur dioxide. Secondly, by modifications of the apparatus, leading to improved control and greater convenience in working. The whole of this work awaits publication, and at the moment no more than the briefest synopsis can be presented. At an early stage, the known relative corrosion behavior of a series of steels of increasing copper content was satisfactorily reproduced and good progress was made in the more difficult task of reproducing the effect of other alloying elements.

The primary objective here is the rapid evaluation of protective coatings. Naturally, the possibility of using the existing accelerated corrosion cycle has been first explored. and a number of modifications have been made, structurally and otherwise. The cycle normally comprises (a) a rust-nuclei forming solution, (b) a dilute sulfuric acid spray, and (c) a humid sulfur dioxide-containing atmosphere. This has given reasonable correlation with data from open-air tests in the industrial atmosphere, with an acceleration factor of the order of 20:1. The method has the advantage of adaptability, since the spray system can be readily modified to simulate any particular type of environment. Quite recently, for example, it has been used to reproduce the corrosive effects of the atmosphere in the neighborhood of Bombay.

The Section has participated in a collaborative scheme sponsored by the Methods of Testing (Corrosion) Sub-Commitee of the Iron and Steel Institute (now of British Iron and Steel Research Association). Use is

made of a simple portable spray apparatus developed by S. G. Clarke (ARD, Woolwich) and the specimens receive artificial mechanical damage prior to the corrosion test. For this purpose, a simple form of indentation machine has been devised.[10] This inflicts upon the specimen a controlled local deformation, which for the purpose of the specification is supplemented by two standard scratches just penetrating the paint coating. Breakdown of the coating is facilitated at the sites of the damage and the performance of the coating is assessed in part by the rate at which rusting develops at these sites.

The investigation on accelerated atmospheric tests now proceeding in the Section includes the development of a relatively simple accelerated test in which moisture films are precipitated from a heated atmosphere containing small amounts of sulfur dioxide. The apparatus is compact, a battery of such vessels being operated without difficulty. A relatively high acceleration factor is achieved without departing unduly from principles that have been established for corrosion in industrial atmospheres.

Methods of Pre-treatment

Of available methods of pre-treating steel those depending on some form of phosphating are the best known and are at present widely used industrially, particularly for surfaces intended for atmospheric exposure. An investigation into phosphate coatings, with special reference to methods for rapidly appraising the properties and efficiency of such coatings, was initiated at the request of Ministry of Works. Good progress can be said to have been made, first in the investigation of characteristics, both physical and chemical, of phosphate coatings on which their efficiency depends, and for which simple methods of measurement are possible; secondly, in the development of a satisfactory performance test that will integrate all such characteristics in respect to resistance to corrosion, either of the phosphate coating itself or the coating system of which it forms an integral part.

Turning to methods of pre-treatment for under-water protective systems, two main lines of experimental technique are being followed. The first consists in plotting potential-time curves over unusually long times, for painted and unpainted ship plate, when immersed in sea water, with and without the pre-treatment under investigation. The curves show well-defined stages, the periods of inflection being related to the protective value of the coating. Still more sensitive indications of the period of breakdown of a coating are given by changes in electrical capacity and resistance of the painted plates, as measured with alternating current of frequency 1000 cycles per second. In parallel with these electrochemical measurements, the high-speed rotor technique is being employed; this constitutes, as might be supposed, a very efficient test for the adhesion of a protective system, and the two methods of examination are converging satisfactorily.

The work as a whole strikingly exhibits the value and importance of pre-treatment of the metal surface since it is a common experience for a suitable pre-treatment to

change the rating of a given protective system from "poor" to "very good."

Microbiological (Soil) Corrosion

Enormous economic importance is attached to corrosion of metals buried in the ground. A remarkable feature is that failures commonly occur in heavy clay soils under conditions such that access of atmospheric oxygen to the metal is fairly effectively prevented. This constitutes somewhat of a paradox because, as we have seen, such access of oxygen is normally required and is a common controlling factor under immersed as distinct from buried conditions. The solution of this paradox was found by Von Wolzogen Kuhr in Holland and by H. J. Bunker at Chemical Research Laboratory.[11] It lies in the action of anaerobic sulfate-reducing bacteria, *Vibrio desulphuricans,* commonly abundant in clay soils, which also normally carry the necessary inorganic sulfates. The important conclusion was reached that these organisms are able, by reducing sulfates in the neighborhood of the metal, to render the oxygen of the sulfate available for cathodic depolarization of the "corrosion cell." The net result is that although oxygen is nominally excluded, it is actually provided *in situ,* just where it is needed for corrosion.

In the case of cast iron pipes, this characteristically takes the form of so-called graphitization, the external from of the pipe being remarkably maintained. At the places affected the graphitic residue is sufficiently soft to be cut with a knife, or even to be scratched with the finger-nail; mechanically, of course, it is useless, so that when the process has gone sufficiently far a burst pipe results; this may occur in extreme cases in as short a time as a year. From the corrosion point of view, the phenomenon provides an interesting case of a controlling factor that is not found at all in ordinary aerobic corrosion. It opens up, in fact, an entirely new field of inquiry which, although certain analogies may be drawn, presents quite different problems from those of either immersed or atmospheric corrosion. Purely microbiological problems which are under investigation include the growth factors of the organisms, the study of various culture methods, the search for suitable bacteriostatic or bactericidal agents and for other anaerobic organisms which might play a similar part in stimulating corrosion. The mechanism of the corrosion process itself under these anaerobic conditions is presenting a most fruitful field for fundamental study.

The more immediate problems of microbiological soil corrosion are being approached in three ways: (1) by laboratory experiments under controlled conditions; (2) by semi-scale experiments under natural conditions; (3) by experiments in the field, with the collaboration of appropriate outside organizations. Here, the invaluable cooperation already received from several water authorities is acknowledged. In particular, the Metropolitan Water Board laid down a number of experimental stretches of water mains at a large new housing estate incorporating several different protective schemes; this is obviously a very long-term experiment.

Another aspect of this work is

that of giving advice whether a buried pipeline should be protected or not. Fortunately, not all soils are aggressive and it is possible to judge within limits from an examination of the soil whether or not microbiological corrosion is likely to occur. However, the criteria by which the aggressiveness of a soil should be judged are by no means fully established, and much further investigation is required.

It is known that sulfate-reducing bacteria may cause similar damage in quite a different environment, namely, that of the sea, the essential condition for their activity again being the exclusion of oxygen. Evidence is accumulating that they are responsible for at least some of the corrosion encountered on ships' hulls, where they find suitable anaerobic conditions underneath the growths of fouling organisms which collect in certain waters on the submerged surfaces. This problem also is receiving attention in the Microbiological Wing of the Corrosion Section.

Information Services

There is maintained in the Section a card index Bibliography of Metallic Corrosion which, since 1928, has incorporated some 30,000 entries, with some 17,000 author entries. This bibliography is used in dealing with many technical inquiries which reach us either directly or indirectly from industrial concerns. Another use is in the preparation of Sectional Bibliographies dealing with corrosion in some branch of industry, and these have been supplied on a number of occasions.

One sometimes hears comparisons made, not altogether uninvidiously, on the prosecution of research in government laboratories, in industry, and in universities. Without particular reference to corrosion, I should like to express my conviction that good team work and the true research spirit are not the prerogatives of any one type of institution. For our part, in the atmosphere of greater freedom that we share no less than others, we intend to continue in the "joy of the chase."

References

1. Vernon, W. H. J., Trans. Inst. Chem. Eng. **17,** 171 (1939).
2. Bengough, G. D., Wormwell, F., Yardley, V. A., Nurse, T. J., B. P. 569,342/45 (Application, 1942), "Improvements Relating to Apparatus for Testing the Corrosion Resistance of Metals, Metallic Coatings, Etc."
3. Vernon, W. H. J., Wormwell, F., Stroud, E. G., Ison, H. C. K., B. P. Application No. 22493/45, "Improvements in or Relating to Media for Use in Heat Exchange Systems."
4. Vernon, W. H. J., Wormwell, F., Nurse, T. J., J. Iron and Steel Inst. **150,** 81p (1944).
5. Vernon, W. H. J., Wormwell, F., Lewis, J. A., B. P. 578,847/45 (Application, 1941), "Improvements in or Relating to De-Icing Fluids."
6. Vernon, W. H. J., Stroud, E. G., B. P. Application No. 13,320/44, "Improvements in or Relating to Packaging."
7. Stroud, E. G., Vernon, W. H. J., B. P. Application No. 18,824/45, "Improvements in or Relating to Packaging."
8. Vernon, W. H. J., Chem. and Ind. **62,** 314 (1943).
9. Swinden, T., and Stevenson, W. W., J. Iron and Steel Inst. **142,** 165p (1940).
10. Preston, R. St. J., and Phillips, C. E., B. P. Application No. 18,998/46, "Indentation Apparatus for Testing Protective Coatings."
11. Bunker, H. J., Jour. Soc. Chem. Ind. **58,** 93 (1939).

Mechanism of Oxidation and Tarnishing

*By Ulick R. Evans**

Dr. Ulick R. Evans' paper is reproduced here by courtesy of The Electrochemical Society. The paper was presented at the Ninety-first General Meeting of the Society in Louisville, Ky., April 9-12, 1947. In recognition of his contributions in the science of corrosion, the National Association of Corrosion Engineers this year designated Dr. Evans to receive the Willis Rodney Whitney Award in the Science of Corrosion. Presentation will be made during the Annual Conference and Exhibition of NACE at Hotel Jefferson in St. Louis, Mo., April 5-8.

Introduction

Experimental Facts. Three equations have been established defining the mean thickness of oxide, y produced after an exposure lasting time t. These are:

	Differentiated Form	*Integrated Form*
The rectilinear equation	$dy/dt = k_1$	$y = K_1 t + K_2$
The logarithmic equation	$dy/dt = k_2 e^{-k_3 y}$	$y = K_3 \log (K_4 t + K_5)$
The parabolic equation	$dy/dt = k_4/y$	$y^2 = K_6 t + K_7$

The relations between the constants (k_1, k_2, etc.) of the differentiated forms and those of the integrated forms (K_1, K_2, K_3, etc.). chosen to represent both sets in the simplest manner, are

$$K_1 = k_1$$
$$K_3 = 1/k_3$$
$$K_4 = k_2 k_3$$
$$K_6 = 2k_4$$

All these constants vary with temperature, but are independent of time. K_2, K_5 and K_7 represent, or include integration constants.

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The same metal may obey different laws under different conditions. Sometimes it is the conditions prevailing at the outset of exposure that determine subsequent behavior. The main facts, as established by Vernon,[1, 2, 3] Pilling and Bedworth,[4] Dunn,[5] Feitknecht,[6] Rideal and Wilkins,[7] Portevin, Prétet and Jolivet,[8] Vernon, Akeroyd and Stroud,[9] Winterbottom,[10] Dighton and Miley,[11] Bénard and Coquelle,[12] and Lustman,[13] appear to be as follows:

Iron[2, 8, 9, 10, 12] conforms to the parabolic equation over a range above 200° C. and the logarithmic equation below 195° C. At relatively high temperatures the FeO film thickens parabolically, and the Fe_3O_4 and Fe_2O_3 films in a nearly rectilinear manner.

Copper[3, 4, 5, 6, 11, 13, 14, 15] conforms to the parabolic equation around 800° C. About 250° it obeys the parabolic equation at low thickness and the logarithmic equation at high thickness. Copper exposed in London air (fluctuating temperature and humidity with sulfur compounds present) conforms to the parabolic law, at least if exposure starts in summer.

Zinc[1, 9, 13] conforms to the rectilinear equation if exposed under fluctuating conditions to London air, but to the logarithmic equation if exposed to relatively pure air at constant temperature.

Aluminum presents complications and will be discussed later.

Object of Present Paper. No entirely satisfactory derivation of the logarithmic law has yet been given, and few attempts have been made to explain why the conditions at the outset of exposure often fix a corrosion behavior which persists after those conditions have changed, or why a metal can start to oxidize according to one law, and then suddenly change to another.

The aim of the present paper is to discuss these three questions. It will open with a review of the present state of knowledge and the mechanisms put forward in previous papers. A general theory of the breakdown of constrained films will follow, and finally this will be applied to explain the behavior of zinc, copper and aluminum.

Present State of Knowledge

Lattice-Migration Thickening. It is generally agreed that parabolic thickening often occurs when the film substance is a semi-conductor, *e.g.*, as a result of lattice defects associated with a departure from the stoichiometric formula. Such defects make possible the outward passage of metallic cations and electrons which, meeting oxygen at the outer surface, build up upon that surface additional layers of oxide. The fact that films grow outward has been made clear by the experiments of Pfeil[16] and Wagner.[17] It is necessary that both the cation and the electron shall move outwards through the film; otherwise a charge would accumulate. The resistance to the movement of both particles is proportional to y, so that the rate of growth is proportional to $1/y$, giving $dy/dt = k_4/y$, provided that the rate of thickening is controlled purely by resistance to passage through the film.

The constant k_4 is believed to depend on the electrical constants of the film in the manner determined by Wagner's equations[17]—of which an instructive derivation has been provided by Hoar and Price.[18] In the only three cases of film growth where the electrical constants are known (Cu_2O on Cu, Ag_2S

on Ag, and CuI on Cu), the experimentally determined values of k_4 accord well with the values calculated from the electrical data.[19]

Under equilibrium conditions, the number and mobility of lattice defects diminish exponentially as the temperature drops, and the value of k_4 diminishes exponentially also; log k_4 is, therefore, a linear function of 1/T.

Deviations from the parabolic equation are to be expected in the opening stages. The condition for parabolic thickening is that growth is controlled by passage across the thickness of the film; when the film is very thin, the boundary reactions may be unable to keep up with the rapid rate permissible by considerations of migration. In an early paper, the author,[20] assuming "chemical" reaction at the boundary and "physical" diffusion through the film governed by constants k_c and k_p respectively, arrived at the relationship

$$\frac{dy}{dt} = \frac{k_p k_c C}{k_c y + k_p}$$

where C is the concentration of the diffusing substance. This leads to an equation of the type

$$K_p y^2 + K_c y + K = t$$

which Fischbeck's experiments[21] afterwards showed to be obeyed by steam acting on iron. The equation reduces to the rectilinear $K_c y + K = t$ at small values of y and to the ordinary parabolic equation $K_p y^2 + K = t$ at large values. Experimental work with Bannister[22] showed that the formation of iodide films on silver, which obeys the parabolic law at great thickness, seems to follow a roughly rectilinear course at low thicknesses.

At very low oxygen concentrations, the boundary changes may fail to keep up with the rate made possible by considerations of migration even at high thicknesses—explaining the departure from the parabolic relation noted by Wilkins and Rideal[7] in the oxidation of copper at low oxygen pressure.

Mott[24] has suggested another cause of departure from the parabolic form at low thicknesses. Ionic mobility is no longer constant in strong fields such as probably exist in very thin films, and this leads to an equation of the form

$$dy/dt = k \sinh (k'/y)$$

Another important cause of irregularities in the early stages becomes apparent if it is remembered that changes tend to start at nuclei and spread out therefrom. The equations to be expected if oxidation starts at nuclei on the oxide-free surface and extends laterally have been worked out by the author.[25] The uncovered fraction of the surface should be represented by $K_8 e^{-K_9 t^2}$ if the nuclei are randomly dispersed over the surface and become operative in all cases at $t = 0$; but by $K_{10} e^{-K_{11} t^3}$ if the appearance of nuclei is random in respect of time as well as position. Both expressions lead to sigmoid curves representing the relation of the coverage to time. Sigmoid forms for the oxidation of copper have been established by Wagner and Grunewald[14] and by Bangham,[15] and are probably caused by lateral growth superimposed on growth in depth. Lateral growth is only important in the "opening stages" of a film-forming process, but in some cases, notably in the spreading of rust patches from centers on iron exposed to damp air, the opening stages may last many weeks. Some of Patterson's curves[26] for iron exposed over water show a well-marked sigmoid form.*

* Agar has suggested that in some cases sigmoid growth may be due to the development of cracking.

Evidence in favor of lateral growth has been provided by Phelps, Gulbransen and Hickman,[23] mainly through examination with an electron microscope of oxide films stripped from nine different metals by the method of Stockdale and the author.[34] Phelps and his colleagues state that the first stage of the reaction of a clean metal involves the formation of a monomolecular layer, after which "at some point crystal nucleation must start and then the crystal must grow. Its growth in the surface plane is limited by the interference of other crystals."

Agar has suggested another reason for the deviation from parabolic growth in the early stages; on a rough surface the metal/oxide interface will straighten out as the film thickens, and, since the area involved is not constant, a departure from the law must be expected.

Complications Due to Cracking.

Lowering of temperature, although unfavorable to lattice migration, may render the film substance brittle; if cracking occurs, this may either *help* or *hinder* oxidation, according to circumstances.

Pilling and Bedworth[4] found that copper exposed to oxygen at 800° C. furnished a smooth curve representing the parabolic equation; at 500° C., oxidation started as a smooth curve (rising less rapidly than that obtained at 800° C.), but at a certain moment oxidation, which had become relatively slow, suddenly became rapid again, evidently because the film had cracked. (See Figure 1.) Similarly, aluminum, in Vernon's tests[1] carried out in London under variable conditions of temperature and humidity, first showed a rapid weight increase, which gradually slackened; then suddenly, after oxidation seemed to have ceased, the specimen started to increase in weight again, in a manner suggesting that the film had cracked.

In certain other cases, however, instead of a sudden *increase* in oxidation rate, a sudden *decrease* is met with. Dighton and Miley[11] found that copper exposed at 225° C. first obeyed accurately the parabolic law, but at a certain moment the rate *suddenly* became slower, subsequently obeying the logarithmic law. The two limbs of the curve cut at an angle.

In the three examples quoted, the sudden alteration in rate occurred only on rare occasions, so that discontinuous curves were produced. If, instead of a few abrupt changes, there were to be a succession of numerous small changes, an almost smooth curve would be expected, obeying a new equation. In this way it is possible to arrive at an explanation of the logarithmic law. The view developed below contains much in common with the author's earlier derivations of that law,[27, 28, 29] but incorporates certain new suggestions made by Orowan, founded upon his experiences in the cracking of mica[30]; these remove many of the difficulties attaching to previous treatments.

Evidence of Alternate Cracking and Healing.

Microscopic study of films separated by the author[31] from heat-tinted iron in 1927 suggested that "the thickening of the film with time may be due rather to the passage of oxygen through the continually opening cracks than to diffusion through the substance of the films. . . ." Later, Britton[32] obtained definite indications of alternate

cracking and healing during the corrosion of an aluminum anode in phosphate-chromate or chloride-chromate solutions. In chloride-chromate solutions, the potential at a given point fluctuated wildly with time; the variation evidently represented local breakdown followed by repair; the current-time curve was relatively smooth, since the current represents the average result of breakdown and repair at a *large number* of points. Even the current-time curve showed fluctuations when corrosion was concentrated at a *limited number* of points. In a phosphate-chromate bath, one specimen, which developed a small number of pronounced pits, showed violent fluctuations of current with time, while another specimen, which was uniformly attacked, provided an almost smooth curve, evidently owing to the "averaging out" of the phenomena at different places.

Recently information has been obtained by the author[33] from a study of rust spots. Heat-tinted steel was engraved with scratch-lines and exposed to air for a suitable period; then filter paper soaked in a solution containing sodium carbonate and bicarbonate at a concentration representing the border-line between activity and passivity was brought into contact with the surface. Rust spots appeared on the filter

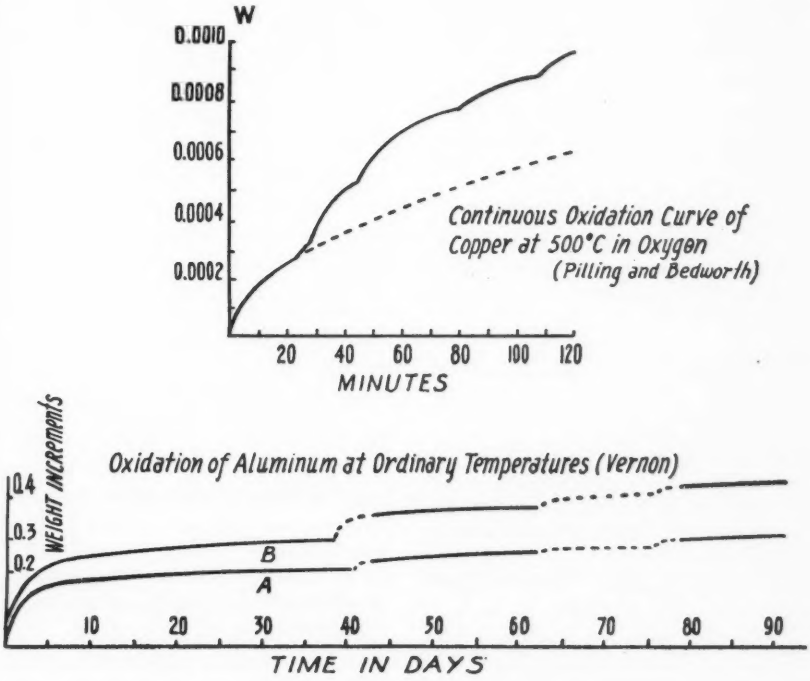

Figure 1

paper,* representing the larger discontinuities, since rust can be formed only where the rate of effusion of iron cations exceeds the rate of arrival of inhibitor anions; thus a concentrated solution develops rust spots only at exceptionally large pores (precipitating iron carbonate *within* the small ones and blocking them up), whereas a dilute solution can show up the smaller pores also.

When a specimen, after leaving its "pattern" of rust spots printed on filter paper, was dried, exposed to air, and again "printed," most of the old spots were found to have disappeared, but some fresh ones had appeared at new places; on immersion in the solution and fresh printing, further new spots appeared. The production of new spots was not due to the action of the liquid as such, but was an after-effect of the air-exposure; for a sequence of exposures to liquid, with intervening printings, was found to produce a pattern of spots which soon became almost constant. These and other experiments support the view that the *primary* effect of oxygen-exposure is to *heal up* the original discontinuities in the invisible oxide film, but the *secondary effect* is to *produce new discontinuities.*

Evidence of Lateral Compression in Films.

Since the unconstrained volume of oxide is (except for very light metals, such as sodium and magnesium) greater than that of the metal destroyed in producing it, a freshly formed oxide film is often found to be in a state of lateral compression. Ocular evidence of lateral compression was obtained by Stockdale and the author[34] during the isolation of the films by anodic undermining of the metal on which they rested; as they became loose, the films wrinkled up, showing that previously they had been occupying an unnaturally small area. In later cases studied at Cambridge the films separated from metal rolled up into tight rolls suggesting that the internal stress in the outer and inner layers must have been different. Occasionally copper plates when heated suddenly throw off little saucer-shaped fragments of scale, but the internal stress (of which the shape gives evidence) is in this case probably due to the relation between the molecular volumes of cuprous and cupric oxides.

Electron diffraction studies by Finch and Quarrell[35] on sublimed zinc (which consists of very perfect crystals, as shown by Straumanis[36]) suggested that the first-formed portions of the zinc oxide are pseudomorphic after metallic zinc, which implies that the oxide lattice is abnormally short in the direction parallel to the surface and abnormally long at right angles (6.79A instead of 5.18A), the cell volume being hardly changed. Later the structure passed to that of normal undistorted zinc oxide; presumably some "stress-relief process"—such as that suggested below—had taken place. This seemed to afford evidence of lateral compression at the base of the film, but Shearer (reported by Vernon, Akeroyd and Stroud[9]) failed to find pseudomorphic material on abraded sheet, possibly because the crystal structure at the surface of the metal was itself somewhat imperfect.

It is sometime argued that the mechanism of oxidation advanced by

* It was convenient, after removing the filter paper from the metal, to convert the rust into Prussian Blue, by soaking in potassium ferrocyanide solution thus making the spots more conspicuous.

Pfeil[16] and Wagner[17] should not lead to a film in lateral compression. If film growth depended *entirely* on movement of cations outwards, this might well be the case, but neither Pfeil's experiments nor Wagner's theoretical reasoning precludes *part* of the movement being due to movement of anions inwards. The existence of vacant places on anion as well as cation lattices is well recognized and is brought out in recent work by Anderson and Richards[37] on lead sulfide.

Probably, however, the passage of oxygen or other non-metal into the metal occurs in the opening stages of oxidation, producing an abnormal structure which, once started, is continued. The first step is doubtless the attachment of oxygen by van der Waals forces, but this physical adsorption must soon pass into chemi-adsorption. Later oxygen begins to diffuse into the metal itself, giving what is in effect a solid solution of oxygen in metal. Evidence of this diffusion in solid solution is provided by the work of Rhines[38] and others on subscales. Smith,[39] discussing the oxidation of a copper-silicon alloy, alludes to the existence, below the oxide film proper, of a layer containing silica particles embedded in a matrix of metallic copper; the sharp demarcation of this subscale (or "zone of internal oxidation") is made very clear by Jacquet's beautiful color photographs[40] of anodically polished microsections tinted with ammonium sulfide.

Presumably when the concentration of oxygen below the surface of an (unalloyed) metal exceeds a certain value, the solid solution becomes metastable, and oxide appears as a new phase. At the moment of formation, this must occupy the space previously occupied by the solid solution, which is less than would correspond to the normal density of the oxide. In the direction at right angles to the surface, the atoms can move outwards, relieving the compression; in the direction parallel to the surface they cannot move; thus lateral compression remains, and the crystal architecture of the oxide is a constrained and unnatural one. If at this stage the movement of cations outwards through the film takes place, they are likely to continue the building of the crystal on the same unnatural parameter, until the accumulating strain energy leads to breakdown in one of the ways suggested below.

There may, of course, be other causes of internal stress in films. Experimental work now in progress on the transfer of oxide films from nickel to a soft vaseline bed suggests that internal stresses left after the abrasion of the metal can play a part in causing the transferred films to break, curl up and peel off. Such observations may be useful in explaining why on roughened metal passivity breaks down more easily than on a finely-finished surface, but it is doubtful whether internal stresses present in the metal play any very important part in the mechanism of oxidation. Film stresses derived from residual stresses present in the metal before oxidation will not be considered in the present paper.

Whatever their origin, there is satisfactory evidence of the real existence of stresses in films, and it is next necessary to consider the manner in which a constrained film on a metallic surface can break down under such stresses.

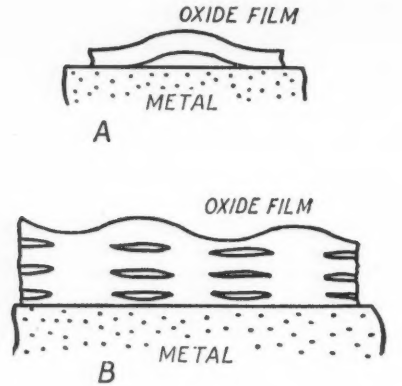

Fig. 2 BLISTERING

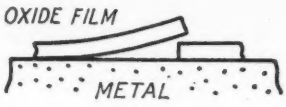

Fig. 3 FLAKING

Fig. 4 SHEAR CRACKING

The Different Mechanisms of Breakdown

General. An oxide film, as freshly formed on metal, may be compared to a compressed spring, except that the compression exists in two dimensions instead of only one. There are three separate ways in which a laterally compressed film can break down, releasing much of its energy of compression. It can form a blister (Figure 2-A), it can break and partially flake off (Figure 3), or it can develop shear cracks (Figure 4). Blistering involves detachment but no real breakage and may be expected where adhesion is poor and cohesion good. Shear-cracking involves breakage but no detachment and may be expected where adhesion is good and cohesion poor. Flaking is likely to be a rare phenomenon, but when once started, to spread rapidly.

I. *Blistering.* The film can rise as a blister, without external work being applied to it, when y reaches a breaking value y_B defined by

$$Qay_BW_C = aW_A \text{ or } y_B = W_A/QW_C$$

where a is the area over which the blister rises, W_A the adhesional work per unit *area*, W_C the compressional work per unit *volume*, and Q the proportion of energy released, which is itself dependent on a, since much strain energy is left in a small (sharply bent) blister.* On small blisters, therefore, Q must be considerably less than unity, but it will approach unity when a becomes large. Nevertheless, if, as is probably the case, W_A varies from point to point, the blisters are likely, in normal cases, to remain very small, being confined to those little areas where W_A is unusually low.

* If the process of detachment involves an "energy hump," the thickness y_B needed for blistering may exceed W_A/QW_C, but in this and analogous cases throughout the paper, the provision of surplus energy to carry the process over a hump is neglected.

Under exceptional circumstances, individual blisters may attain considerable size. Griffiths[41] produced conspicuous blistering on steel heated at about 900° C. in oxygen diluted with nitrogen or carbon dioxide. Such a phenomenon is probably connected with large areas of low adhesion, and, although instructive as demonstrating the manner in which internal stresses lead to individual blisters, may not represent the structure of films containing vast numbers of flat microscopic cavities—one above the other. Evidence of the pastry-like structure of the thinner films present on heat-tinted pure iron was presented in the author's early description of films isolated by the iodine method[31]; "such films when freshly removed showed numerous holes, and beside these holes, or covering them, were smaller pieces of films attached as 'flaps' to the main films."

The formation of blisters may be pictured as follows. In the opening stage of oxidation the metal is covered by a pseudomorphic film in lateral compression. Cations from the metal keep moving outwards through the film, taking their places on the outer face, and forming with oxygen atoms (which are converted to ions by the electrons also moving outwards) an extension of the oxide lattice. Sooner or later, the film will reach the critical thickness y_B corresponding to the value of W_A prevailing at those areas where, for some reason, adhesion is lowest. At such areas, it should be possible for the film to rise as blisters, releasing much of the strain energy (possibly the plane of separation may be a few atomic layers above the actual interface between metal and oxide, since the lowest atoms of the oxide film are anchored to the metal). On the areas covered by blisters, outward migration of the ions must suddenly become slow, since the lenticular space below the blister wall acts as a "cavity-barrier" which they cannot cross, and the alternative route along the walls of the cavity is a relatively long one. The bending of the films will probably produce minor rifts roughly at right angles to the metallic surface, and two cases must be distinguished, according as these are permeable or impermeable to oxygen *molecules.*

(a) *If the rifts are sufficiently broad to admit oxygen molecules* from the atmosphere to the cavity within the blister, the metal below the seat of the blister can build a new film, until once more a thickness equal to y_B has been reached, when fresh blister-formation may be expected. At places of higher adhesion, outward cationic movement continues across the bridges between the cavity barriers, at a diminishing rate, until the thickness reaches the value of y_B corresponding to the local value of W_A, thus making possible the formation of cavities at these places also.

If we neglect the jerkiness due to alternate breakdown and repair, it is clear that growth is rectilinear, the value of k_1 in the equation $dy/dt = k_1$ being connected with the parabolic growth constant k_4 by the equation

$$k_1 = \frac{\alpha\, k_4}{Y}$$

where α is the fraction of the area covered by "active" (oxygen-admitting) blisters at any moment, and where $1/Y$ is the mean of $1/y_P$, averaged *over time*, y_P being the thickness of the *pseudomorphic* layer. Actually, at a given point, the thickness of the

pseudomorphic film will vary between zero and y_B, breaking down whenever it reaches that value. Now

$$\frac{1}{Y} = \frac{\int \frac{1}{y_p}\,dt}{\int dt} = \frac{\int_0^{y_B} \frac{1}{k_4}\,dy_p}{\int_0^{y_B} \frac{y_p}{k_4}\,dy_p} = \frac{2}{y_B}$$

Thus the relation between the constants of rectilinear and parabolic growth should, in the absence of other complications, be given by

$$\frac{k_1}{k_4} = \frac{\alpha}{Y} = \frac{2\alpha}{y_B} = \frac{2\alpha Q W_C}{W_A}$$

which, however, neglects the variation of W_A and y_B from point to point. If this is appreciable we can write

$$\frac{k_1}{k_4} = 2\alpha\,\overline{[1/y_B]} = 2\alpha\, Q W_C\,\overline{[1/W_A]}$$

where $\overline{[1/y_B]}$ and $\overline{[1/W_A]}$ are the mean values of $1/y_B$ and $1/W_A$, averaged *over space.*

(b) *If the rifts in the blister skin are insufficiently large to admit oxygen molecules,* film growth must depend solely on the migration of cations outwards. Across the blisters proper, this is now impossible but the bridges between the blisters may provide favorable paths for the movement of cations. Clearly, however, the area available for cation migration has been reduced by the blistering, thus explaining why breakdown sometimes leads to a sudden retardation in the oxidation rate, as found by Dighton and Miley.[11] As thickening continues, fresh cavity barriers are formed parallel to the surface, so that the area affected by oxidation continually diminishes. At any point which is vertically below a cavity barrier, passage of cations outwards may be negligibly slow. At any point which is not vertically below one of these barriers, the passage of cations outwards can proceed at a pace which is determined mainly by the thickness of the pseudomorphic film; it should be almost independent of the thickness of the outer layers, which have lost most of their lateral compression, and thus offer much less resistance to the passage of cations outwards; the presence of rifts roughly at right angles to the general surface should facilitate the migration of cations across this outer, stress-relieved zone.

The effective rate of thickening at a place where any thickening is occurring at all will thus be represented by

$$2\,k_4\overline{[1/y_B]} = 2\,k_4 Q W_C\,\overline{[1/W_A]}$$

To obtain the effective rate of thickening of the whole surface, we must multiply by the probability that a representative point will not be covered by a cavity barrier. Now if we *define* the chance of a barrier being situated within the thickness element dy as $k_3 dy$, the chance that there will be no barrier in y, the thickness of the *whole* film, must be $e^{-k_3 y}$, provided that k_3 is independent of y (the validity of this condition is discussed later). Thus the equation giving the rate of mean thickening will be

$$dy/dt = 2k_4 Q W_C \cdot \overline{[1/W_A]} \cdot e^{-k_3 y}$$

which can be written

$dy/dt = k_2 e^{-k_3 y}$ or $y = K_3 \log(K_4 t + K_5)$

—the logarithmic equation. It should be noticed that the constant k_2 of the logarithmic equation is closely connected with k_4 and therefore with k_1 (the constants of the other two equations), but that k_3 depends largely on the correlation between the positions of the different cavity barriers. If they are all in register one above the other (Figure 2-B), k_3 will be much smaller, other things being equal, than if they are uncorrelated, as in Figure 2-C.

The existence of a close connection between the principal growth constants of the three equations (k_1, k_2 and k_4) suggests an explanation as to why the growth rate of a given metal seems to preserve the same *order of magnitude,* even though the law of growth changes. For instance, Dighton and Miley's curves[11] on copper show clearly that a change of law occurs at a certain moment. y^2 plotted against t gives a straight line up to that moment, but not after it; y plotted against $\log(t + K_5)$, which Dighton and Miley write $\log(t + t' + \frac{1}{a})$, gives a straight line after the moment but not before it. A straight plot of y against t, however, shows no drastic alteration of slope at the moment of change-over; the ratio of the gradient just before the change-over to that just after it varies from about 1·6 to 4·0 according to the temperature. If there were an abrupt change of mechanism, it would at least be a strange coincidence that the velocity was so little affected. If the mechanism is the same before and after the change-over, the only modification being that part of the cross-section has become unavailable for migration through the screening action of the cavity barriers, there is no cause for surprise.

In the derivation of the logarithmic equation, it has been assumed that the impedance to cations exerted by the stress-relieved portions is small compared to that offered by the compressed pseudomorphic film at the base, so that thickness has no effect on the rate of passage at points not covered by a cavity barrier, but only affects the probability that a point shall be covered by such a barrier. If the stress-relief has been incomplete, or if the upper part of the film has become very thick, this may no longer be true, and even at points where there is no barrier, the rate of passage may fall off as y increases, ultimately becoming proportional to 1/y. The equation should then become

$$\frac{dy}{dt} = \frac{k_4}{y} e^{-k_3 y}$$

giving a curve which at relatively small thicknesses may be roughly parabolic but which falls more and more below the parabola as time increases. If the cavity barriers are in register, so that k_3 is small, we should get an accurate parabola. The same relationship would hold if the pseudomorphic film at the base were absent altogether. Thus the occurrence of cavity barriers does not preclude a parabolic growth law.

Even where stress-relief in the outer portions is complete, a departure from the logarithmic relation is to be expected at thicknesses comparable to y_B. This matter is considered later. Another cause of departure, suggested by Bangham, is that happenings at the "representative point" may be not independent of happenings at neighboring points.

pseudomorphic film will vary between zero and y_B, breaking down whenever it reaches that value. Now

$$\frac{1}{Y} = \frac{\int \frac{1}{y_p}\,dt}{\int dt} = \frac{\int_0^{y_B} \frac{1}{k_4}\,dy_p}{\int_0^{y_B} \frac{y_p}{k_4}\,dy_p} = \frac{2}{y_B}$$

Thus the relation between the constants of rectilinear and parabolic growth should, in the absence of other complications, be given by

$$\frac{k_1}{k_4} = \frac{\alpha}{Y} = \frac{2\alpha}{y_B} = \frac{2\alpha Q W_c}{W_A}$$

which, however, neglects the variation of W_A and y_B from point to point. If this is appreciable we can write

$$\frac{k_1}{k_4} = 2\alpha\,\overline{[1/y_B]} = 2\alpha\, Q W_c\,\overline{[1/W_A]}$$

where $\overline{[1/y_B]}$ and $\overline{[1/W_A]}$ are the mean values of $1/y_B$ and $1/W_A$, averaged *over space.*

(b) *If the rifts in the blister skin are insufficiently large to admit oxygen molecules,* film growth must depend solely on the migration of cations outwards. Across the blisters proper, this is now impossible but the bridges between the blisters may provide favorable paths for the movement of cations. Clearly, however, the area available for cation migration has been reduced by the blistering, thus explaining why breakdown sometimes leads to a sudden retardation in the oxidation rate, as found by Dighton and Miley.[11] As thickening continues, fresh cavity barriers are formed parallel to the surface, so that the area affected by oxidation continually diminishes. At any point which is vertically below a cavity barrier, passage of cations outwards may be negligibly slow. At any point which is not vertically below one of these barriers, the passage of cations outwards can proceed at a pace which is determined mainly by the thickness of the pseudomorphic film; it should be almost independent of the thickness of the outer layers, which have lost most of their lateral compression, and thus offer much less resistance to the passage of cations outwards; the presence of rifts roughly at right angles to the general surface should facilitate the migration of cations across this outer, stress-relieved zone.

The effective rate of thickening at a place where any thickening is occurring at all will thus be represented by

$$2\,k_4\overline{[1/y_B]} = 2\,k_4 Q W_c\,\overline{[1/W_A]}$$

To obtain the effective rate of thickening of the whole surface, we must multiply by the probability that a representative point will not be covered by a cavity barrier. Now if we *define* the chance of a barrier being situated within the thickness element dy as $k_3 dy$, the chance that there will be no barrier in y, the thickness of the *whole* film, must be $e^{-k_3 y}$, provided that k_3 is independent of y (the validity of this condition is discussed later). Thus the equation giving the rate of mean thickening will be

$$dy/dt = 2k_4 Q W_c \cdot \overline{[1/W_A]} \cdot e^{-k_3 y}$$

which can be written

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Orowan has suggested that the assumption of flat cavity barriers parallel to the surface would explain the somewhat puzzling fact that films composed of material which is very hard when tested in bulk are, in effect, very easily scratched off, *e.g.*, with the finger nail. The cavities may also explain the absence or faintness of interference colors on films which thicken by the logarithmic or linear laws—in contrast with the brilliant tints which accompany parabolic thickening, a matter emphasized by Vernon. Although the cavities are narrow compared to the wave-length of light, they are probably broad enough to prevent the film from acting as if it were optically homogeneous. It is sometimes suggested that the variation of thickness from point to point is the cause of the absence of color, but this is unlikely. The possibility of cations moving along the external surface of the film is likely to make the thickness more uniform than would at first sight appear probable. In any case a certain variation of thickness is actually favorable to the production of color, as pointed out elsewhere,[42] since it broadens the interference bands; clearly excessive variation of thickness will weaken the color again.

Logarithmic growth could, however, occur in the absence of cavity barriers. If pores running roughly normal to the metallic surface tend to get blocked by any random occurrence, such as welding up at certain points owing to residual compressional stresses, or by the growth of new crystals across the channels, thus preventing passage, then if the chance of such a blockage in thickness element dy is $k_3 dy$, the chance of escaping blockage in the complete thickness y is $e^{-k_3 y}$, giving $dy/dt = k_2 e^{-k_3 y}$ as the growth law.

II. *Flaking.* The separation of a portion of the film as a flap (Fig. 3) with severance along the greater part of the periphery of the loosened area must liberate a greater fraction of the strain energy than a blister covering the same area, since a single bend will be involved instead of a 4-fold bend; thus, a given value of a will lead to a higher value of Q, but the severance introduces a new energy term, and flaking can only occur when y reaches a value y_F such that

$$Qay_F W_c = aW_A + y_F W_R k \sqrt{a}$$

where W_R is the work of rupture per unit area of fracture section and k depends on the shape of the detached fragment, being $2\sqrt{\pi}$ for a circle (if the length of the hinge-line is neglected) and approximately

$$2\sqrt{\frac{\pi(1+E^2)}{2E}}$$

for an ellipse of axial ratio E. The last term becomes small compared to the others when a becomes sufficiently large, and this suggests that flaking, even when impossible on grounds of energy over very small areas, would become possible if there chanced to be a large area having a small value of the adhesional work W_A. The probability of this occurrence is small, and flaking must be regarded as an exceptional occurrence. Clearly, however, when once flaking has started, conditions become increasingly favorable as the area involved becomes larger, so that the failure should spread out like an explosion wave. Probably flaking is most likely to occur by the joining together of a large number of nearly contiguous blisters.

The best examples of flaking on a large scale are provided by Griffiths,[41] who found that iron exposed to oxygen diluted with steam gave loose films which became completely detached from the metallic basis; here the easy removal of the scale was connected with porosity in its inner portions, which was shown up in photomicrographs.

III. *Shear-Cracking.* When a cylinder of material fails under axial compression between hard plates, the broken pieces are wedges separated by shear-cracks; the subject is discussed by Nadai.[43] In the case of a thin oxide film in lateral compression, anchored to metal at one face only, cone-shaped fragments might be pressed out if the substance were amorphous, but from crystalline substances, the extruded fragments are more likely to take the form of knife-edged wedges (Fig. 4), producing pyramids where they intersect; the exact form is not important. This form of failure is likely to produce a complicated set of primary cracks at about 45° to the surface, and perhaps secondary cracks in other directions. Uniform gliding is impossible, since the relative displacement must be greater near the outer portion than elsewhere, approaching zero at the innermost point (the apex of the wedge).

Such a form of breakdown involves no work against adhesional forces, but requires extensive breakage of the film substance. A wedge can be extruded only if

$$QW_C > kW_R$$

where k depends on the shape of the wedge. Neither y nor W_A appear in this relation, but since k may depend on thickness, there may be a critical value, y_C, which must be reached before cracking can occur. The films will thus grow by alternate cracking and healing.

Shear-cracking is most likely to be met with when the films are strongly adherent or interlocked (conditions unfavorable for blistering or flaking), provided that the film substance is either mechanically weak, or contains numerous flaws. It should be able to occur while the film is still thin and, although a new pseudomorphic film may be formed below the cracked layer, the cracks will probably soon extend downward into it, so that $\bar{y}_P$ (the value of y_P averaged over time and space) should be smaller than in the case of blister-formation. On the other hand, Q must be much smaller than in the two other forms of breakdown, since although most of the strain energy may be relieved at the outer protruding part of the extruded wedges, there can be practically no relief near the inner apices. Consequently, this form of breakdown is only likely to be met with when W_R is low and W_A high. Since the walls of the shear-cracks must (at least in the region nearest the metal) remain tightly pressed together, the entry of oxygen molecules is normally improbable, but the crack network offers favorable paths for the passage of cations outwards. Since $\bar{y}_P$ may often be small compared to y, it is necessary to consider whether the resistance offered by the pseudomorphic layer to cation movement outwards is large or small compared to that of the outer layer. If it is large, the rectilinear growth law must prevail. If it is small,

the parabolic growth law $dy/dt = k_4/y$ should be obeyed. Where the resistances of the two layers are comparable, an intermediate law is to be expected.

Intermediate relationships may occur in absence of cracking when the conditions favor very rapid passage of cations through a film, without a correspondingly rapid rate of replenishment of oxygen. For instance, Taylor and Cobb[44] found that the weight increase (W) of iron due to oxidation at high temperatures by gas mixtures containing sulfur compounds obeyed the law $W^n = Kt$, where n varied from 1 to 2, increasing with temperature and sulfur content. Sulfides contain more lattice defects than oxides. This is illustrated by the formula $Fe_{11}S_{12}$ assigned in mineralogical textbooks to pyrrhotite; X-ray work by Hägg and Sucksdorff[45] shows that pyrrhotite is really ferrous sulfide, FeS, with 1/12 of the cation sites vacant; 1/6 of them must be occupied by $Fe^{\cdots}$ instead of $Fe^{\cdot\cdot}$ ions. If the number and mobility of lattice defects increases either with rise in temperature or sulfur content, the gradual passage from the rectilinear law ($n = 2$) to the parabolic law ($n = 1$) is easily understood.

In the formation of iodide films on silver placed in a solution of iodine, as studied by Bannister and the author,[22] there is evidence that the cracks responsible for the parabolic thickening obtained are broad enough to allow an inward movement of iodine. If the growth were due simply to outward movement of cations, the concentration of iodine in the external solution should affect the velocity to a comparatively small extent, since parabolic growth is only to be expected when the boundary reactions exercise no control. Actually the rate of growth of silver iodide films was found to increase *rapidly* with the concentration of iodine in a chloroform solution, the effect of iodine concentration being far more marked than the effect of oxygen pressure on the oxidation of metals under conditions where the parabolic relationship holds good. The facts can only reasonably be explained by assuming the surface migration of iodine inwards along the walls of the rifts. The fact that the films show bright interference tints, extending over five orders, is probably connected with the fact that the cracks are not parallel to the surface, and are narrow compared to the wave-length of visible light. Slight internal defects are actually favorable to the production of color.[42]

Bircumshaw and Everdell[46] showed that copper placed in a solution of iodine in aqueous potassium iodide obeyed the rectilinear law if special precautions were taken to keep the concentration constant; here also the iodine moved inwards, not the metal outwards.

In one important case, the cracks threading the outer layer are likely to be sufficiently broad to admit oxygen molecules. This occurs when the stresses are not compressional but tensional. In the case of the alkali and alkali-earth metals, the relationship between densities and atomic weights is such that the unconstrained oxide occupies a volume *less* than the metal destroyed in producing it; the oxide film is, therefore, fluffy and visibly porous, which explains why these metals burn in air. Dunn and Wilkins[47] suggest that here the rate

of attack at constant temperature is likely to be controlled by passage through a thin pseudomorphic layer at the base, which keeps breaking up as the cracks extend inwards, but which is constantly renewed. Pilling and Bedworth[4] found a constant oxidation rate for calcium at 500° C. Magnesium, studied by Gulbransen[48] and by Leontis and Rhines,[49] also obeys the rectilinear law under some conditions, but the mechanism is more complicated; at high temperature, the magnesium vaporizes and diffuses outwards as gas, sometimes combining with oxygen to produce well-formed little cubes of magnesium oxide. Leontis and Rhines' statement that "when the protective scale reaches a certain thickness, it disintegrates spontaneously" suggests that this case will be found to fall into the general scheme.

Application to Individual Metals

General. An explanation has been offered for the fact that the breakdown of a film may cause either a sudden increase or a sudden diminution of the rate of growth, and may replace parabolic thickening by rectilinear thickening, logarithmic thickening or fresh parabolic thickening, according to the nature of the breakdown. It is now possible to apply the general principles developed to the behavior of individual metals, with special reference to the results of Vernon. Iron will not be considered, since most of the experimental results available are based on steel, which contains manganese in solid solution, and cementite as a second phase.

Zinc. Vernon's measurements for the weight increase of zinc exposed indoors in London[1] fall on straight lines, which, when produced backwards, do not pass through the origin —a feature indicating that the velocity at the outset must have been higher than the constant rate finally established. The value of this constant rate seems to depend on the weather conditions prevailing at the outset. Each of his four plates first exposed on Jan. 29, April 24, May 12 and Aug. 19, 1925, respectively established a constant rate of its own; the specimen first exposed on Jan. 29 gained weight more slowly than that first exposed on May 12, maintaining its slow velocity throughout the whole period during which the specimen of May 12 was gaining weight at a higher rate.

The probable cause is as follows: The presence in the film of a small amount of some foreign body (*e.g.*, basic sulfate) will affect the adhesion of oxide to metal. The formation of blisters and hence of barriers will occur on areas where W_A is low, and the extent of these areas must vary with the amount of foreign matter present in the opening stages. Now as the oxide grows outward it will surround the foreign particles, which will remain buried at the base of the film; that this really happens is shown by Pfeil's well-known study[16] of the oxidation of steel previously painted with a distemper of chromic oxide, the grains of which were afterwards found at the *base* of the oxide scale. If, through rifts in the walls of the first blisters formed, oxygen can gain access to the cavities below, a new film will begin to grow below them; the foreign matter will again remain at the base of these second films and, when the pseudomorphic film has reached the appropriate thickness, will lead to the formation of a second series of cavities occupying the same

areas. In this case, the various cavities will be formed one below the other, and the rate of oxidation will remain roughly constant. It will of necessity be less than the rate at the outset, but will be decided by the atmospheric conditions prevailing at the outset, since these conditions decide the areas of exceptionally low W_A. Thus the experimental results receive a simple explanation.*

In contrast to the results in London, Vernon's experiments with Akeroyd and Stroud[9] in closed vessels and under constant conditions at Teddington obeyed the logarithmic law. Presumably the absence of foreign substances rendered the film substance less brittle, so that the walls remained free from rifts large enough to admit oxygen molecules to the internal cavities; under such circumstances, thickening must have depended on the migration of cations moving outwards along the oxide bridges between the cavities, thus explaining the logarithmic relationship. Any minor rifts running at right angles to the surface would aid the movement of zinc ions outwards, but cavity barriers parallel to the surface would have the opposite effect, greatly adding to the length of the path along which the ions must move in order to reach the outer surface of the film.

The curves show marked deviation from the logarithmic law at low thicknesses. This is in no way surprising. A necessary condition for logarithmic thickening is that k_3 should be independent of y; at thicknesses comparable to y_B, this will not be the case. Indeed, if the value of W_A were the same at all points, the cracking would be confined to levels which are exact multiples of y_B. If, however, W_A varies from point to point, the law may be obeyed when the film attains sufficient thickness. It is important to consider at what thickness this obedience may be expected to start.

If the standard deviation of W_A is ζW_A, the standard deviation of the positions of the *lowest* set of cavity barriers from their mean level should be $\zeta \bar{y}_B$, where $\bar{y}_B$ is the modal value, and the variance $\zeta^2 \bar{y}_B^2$. Since the level of the second set of cavity barriers is determined by the already fluctuating level of the first set, the fluctuation of the level of the second set will be greater, and that of the third set greater still. Variance is additive, and if distribution is normal, it would seem that the variance of the position of the cracking at the second, third and fourth levels should be 2, 3 or 4 times $\zeta^2 y_B^2$, so that the standard deviation should be $\sqrt{2}$, $\sqrt{3}$ and $\sqrt{4}$ times $\zeta \bar{y}_B$.

If ζ is very small, the probability of cracking at different distances from the metal-oxide interface would be represented by a series of slender distribution curves, with modes at $\bar{y}_B$, $2\bar{y}_B$, $3\bar{y}_B$, etc. If ζ is large, then the

* It is worth considering whether the "breakaway" of the oxide film on zinc might not be due to moisture as much as to sulfur compounds. The solubilities of zinc oxide and hydroxide are not very different. In presence of liquid water, Warner[50] considers that the hydroxide is the less soluble, and therefore the more stable. There are, moreover, a number of forms of the hydroxide; and also of the basic salts, as shown by Feitknecht and his colleagues.[51] If at some point the oxide passes into solution into a film of condensed moisture, a nucleus of the less soluble hydroxide (or a basic salt) may be deposited, and the transition from the protective pseudomorphic film to nonprotective matter may then proceed apace; any pseudomorphic oxide formed subsequently, at such points will doubtless rapidly undergo the same transformation. But if this were the mechanism, it is not clear why the transformation should not spread out laterally, giving a rate of oxidation which increases with time until the whole is covered. On iron this increasing rate—almost certainly connected with the lateral extension of secondary rust—is met with under some circumstances; but not apparently on zinc.

distribution curves must soon begin to overlap, and the net probability of cracking should become fairly uniform at a short distance away from the interface. Fig. 5-A shows curves corresponding to $\check{s} = 0{\cdot}2$ a value which represents no unusual degree of variation, since it signifies that over two-thirds of the area, the adhesional work lies within 20% of its mean value. The modes of the curves lie at $\bar{y}_B$, $2\bar{y}_B$, $3\bar{y}_B \cdots$, their standard deviations being in the ratio 1, $\sqrt{2}$, $\sqrt{3} \cdots$, while their modal ordinates stand in the ratio 1, $1/\sqrt{2}$, $1/\sqrt{3} \cdots$, so that the area shut in below each curve is the same. The curve B, representing the probability of cracking, is obtained by summing the individual distribution curves; it is wavy at low thicknesses, but levels out at higher thicknesses. Curve C represents the integral $\int \phi dy$ where ϕ is the ordinate of curve B. A necessary condition for obedience to the logarithmic law is that curve C should have become straight, since only then has the expectation of cracking (represented by $k_3 y$ in the logarithmic equation) become proportional to y (in other words, k_3 has become independent of y). It will be seen that the curve C is nearly straight after the second mode of curve A, although a slight waviness is traceable up to the fourth mode. At higher values of $\check{s}$, the curve would straighten at a still lower thickness and it seems reasonable to expect approximate obedience to the logarith-

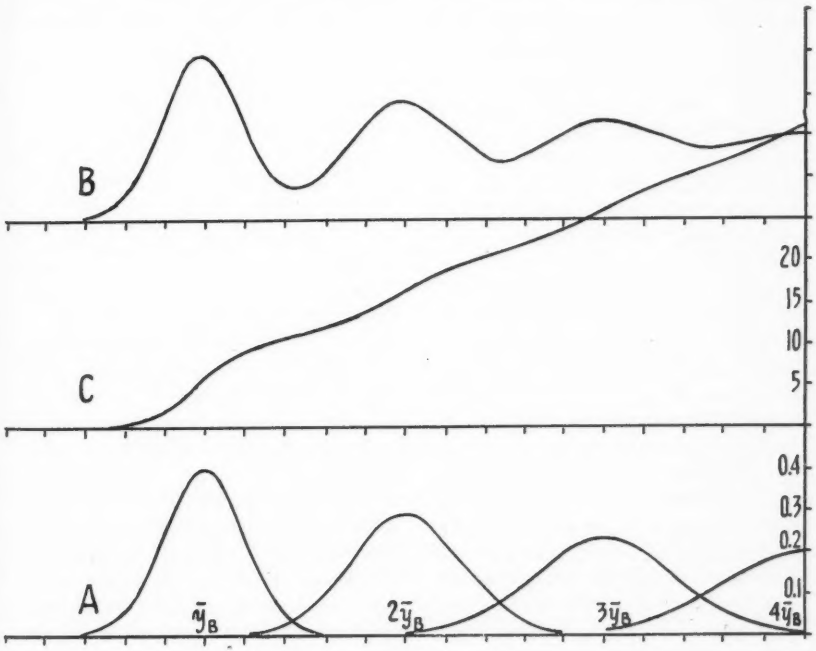

Figure 5

mic law at a thickness round about $2\bar{y}_B$.

Orowan has expressed the opinion, based on calculations from surface energy, that the value of $\bar{y}_B$ would be below 10^{-6}cm. The actual curves determined by Vernon, Akeroyd and Stroud[9] for various temperatures showed that on zinc obedience to the logarithmic law started after a weight increment of about 0·1 to 0·15, mg./dm.^{2} according to the temperature; this corresponds to a film thickness of about 90 to 140A, if the metal was free from oxide at the moment of the first weighing; otherwise it may represent a considerably greater thickness. Assuming a reasonable degree of variation in W_A, the experimental figures appear entirely consistent with Orowan's calculations.

It should be pointed out that, even if δ were known, it would not be possible to calculate k_3, since this contains a factor representing the correlation between the lateral positions of the various sets of cavity barriers. In other words, k_3 depends on the variation of the chance of detachment, not only in space, but also in time.

The curves of Vernon, Akeroyd and Stroud[9] show that in the range 50° to 225° C zinc behaves differently according to its surface preparation. A surface annealed and then etched oxidizes more quickly than one etched in the as-rolled state. Presumably in the latter case the preferred orientation of the metal would be preserved in the pseudomorphic oxide, whereas in the oxide formed on the annealed zinc there would be abrupt changes of orientation; this might well have affected the extent of the cavities, and therefore of the area of the bridges between them. Abraded surfaces were found to experience a smaller rate of increase in weight in a given time than etched surfaces—possibly because they carried a thicker oxide layer at the start of exposure. This interpretation of the effect of surface condition is consistent in principle with that suggested by the Teddington authors.

A remarkable feature of the Teddington curves is the variation of oxidation rate with temerature. In the range 100° to 225° C, the rate increased only very slowly with temperature on abraded, annealed or as-rolled zinc, and actually decreased in the case of zinc which had been annealed and etched; Lustman[13] has provided evidence that on copper the rate falls with rising temperature in the range 105° to 120° C. It is not easy to explain a fall of velocity with rise of temperature on ordinary ideas of kinetics, but on the cracking mechanism it is always possible that a rise of temperature, while increasing the rate of migration of cations per unit area of bridge, may, by increasing the sideways extension of the cracks, greatly decrease the cross-section of the bridges, and so retard oxidation.

Copper. It is well known that copper exposed to air containing hydrogen sulfide develops the same sequence of tints at ordinary temperatures as are produced at elevated temperatures in pure air; presumably, as in the case of iron, a lattice containing sulfur will contain more defects capable of facilitating cation passage outwards than a pure oxide lattice. Vernon[1] showed that the rate of change depends on the amount of reactive sulfur present in the air (*i.e.*, the sulfur capable of reacting with alkaline lead acetate), and that preliminary exposure to pure air (free from sulfur

compounds) diminished the tendency to tarnish when the surface was afterwards brought into air containing sulfur compounds. Conversely, when copper which has been tinted by exposure to air containing hydrogen sulfide is placed in a vessel containing relatively pure air, the interference colors continue to alter in a sense which indicates that the film is continuing to grow—presumably by the uptake of oxygen.

The close obedience to the parabolic law shown, whether the film consists of oxide, sulfide or both, suggests that the form of breakdown is here shear-cracking. The value of k_4 in mixed films naturally increases with the sulfur content; Vernon's measurements show it to be nearly proportional to the content of reactive sulfur in the atmosphere.

Even if the atmosphere subsequently becomes free from sulfur compounds, rapid film growth continues. In a general way this can be explained by the fact that less energy is needed to continue a given style of crystal architecture than to start a new one. Suppose that, owing to the presence of sulfur, the oxide already present has an abnormal lattice constant, the crystal is likely to continue to be built with this abnormal parameter, even though the impurity ceases to be provided. To pass gradually from the abnormal to the normal parameter would, in effect, mean a curvature of the lattice, introducing strain energy; a sudden change from one parameter to another is equivalent to the formation of fresh nuclei, which can only occur at places of abnormally high energy.

The apparent contradiction between Pilling and Bedworth's curves on wire at 500° C and those of Dighton and Miley on sheet about 225° C is presumably explained by the occurrence of the catastrophic (flaking) type of breakdown in the former work, so that after each breakdown rapid oxidation was renewed on a roughly parabolic course, whereas in the latter, the blister type of breakdown developed, imposing barriers over parts of the surface, and giving a diminished rate of oxidation according to the logarithmic law. It is possible that the curvature of the wire surface—quite as much as the higher temperature—was responsible for the formation of the type of cracks which admit oxygen to the metal below.

Aluminum. Vernon's plates of aluminum exposed in a basement in London[1] showed at first an increase in weight, but the rate of increase gradually died away, and the weight appeared to be asymptotically approaching a limiting value, when suddenly (about 40 days from the start of exposure in the case of two of his specimens) a fresh increase occurred —evidently due to the film becoming non-protective; the process then repeated itself. (See Fig. 1.) Champion[52] states that Vernon's numbers obey equations of the form $y = K_{12}(1 - e^{-K_{13}t - K_{14}})$, but that the values of K_{12}, K_{13} and K_{14} change sharply after about nine days. These are, of course, asymptotic types of curves.

Mott[53] at one time attributed the slowing down of the oxidation to the fact that electrons can only penetrate the film by the tunnel effect, which is highly sensitive to thickness. So soon as the rate of entry of electrons, which by Frenkel's formula[54] for leakage across an air-gap should be proportional to e^{-ky}, has slowed down, the entry of cations is thought to be pre-

vented owing to the space charge set up. Thus, argued Mott, "we expect a parabolic law of growth up to a certain thickness, of the order $0{\cdot}5 \times 10^{-6}$ cm., and then a rather sudden stop."

The tunnel effect mechanism, however, leads to the ordinary logarithmic equation $dy/dt = k_2 e^{-k_3 y}$, and not to the asymptotic type of curve found by Vernon. Mott's later theory,[24] already mentioned, leads to an equation of the type

$$dy/dt = k \sinh (k'/y)$$

giving curves not strictly asymptotic, since dy/dt only becomes zero when y is infinite.

Mott is, of course, correct in arguing that many equations which are not strictly asymptotic (in the sense that there is some thickness, y^{∞}, which can never be exceeded however large t is made) would nevertheless lead ultimately to values of dy/dt too low to be detected experimentally. Even the parabolic or logarithmic equation predicts very small values of dy/dt when t becomes sufficiently large. However, Vernon's results cannot be explained adequately by the parabolic or logarithmic equation or by Mott's new equation, and seem to suggest a genuine asymptotic relationship.

The mechanism of crack-formation does lead to a truly asymtotic form of curve, if the mechanical strength of alumina is borne in mind. On copper, which forms a weak oxide, cracking, when once started, is likely to recur at short intervals of time, so that a smooth logarithmic curve is obtained. On aluminum, however, the mechanically strong oxide might be expected to resist structural changes far better than copper oxide. Probably the inception of a crack is an infrequent occurrence, and the region affected by cracking does not spread out quickly. After some days of exposure large parts of the area may not have experienced stress-relief, and here the rate of oxidation should be inversely proportional to the thickness of the film. At other points, cavity barriers may have developed, which the cations cannot cross.

We must picture, during these early stages, true parabolic growth continuing on areas where strain has not been relieved, and no growth at all where cracking has developed. This suggests equations for the rate of weight increase. Two cases deserve consideration. We may regard stress relief at one point as exerting no influence on the points around, so that the fraction (α) of the area which has, at time t, escaped stress relief and is thus continuing to thicken parabolically should be $e^{-k_5 t}$. Or it may be that a cavity barrier starting at any "nucleus" spreads out laterally, and that these nuclei keep appearing at random on the ever-shrinking area that has not received stress-relief; in this case—as shown elsewhere[25]—α should be $e^{-k_6 t^3}$. Here k_6 represents $\pi v^2 \Omega/3$, where v is the velocity of radial spread from the nuclei and Ω is the nucleation rate, defined by the statement that the probability of the formation of a nucleus within time-element dt on an area-element δA is $\Omega \delta A dt$. The two mechanisms are expressed respectively by

$$dW/dt = k_7 t^{-\frac{1}{2}} e^{-k_5 t}$$

and

$$dW/dt = k_7 t^{-\frac{1}{2}} e^{-k_6 t^3}$$

where W is the weight of the specimen at time t; k_7 is related to the usual con-

stant k_4 of the parabolic law, being equal to $\sqrt{k_4}\ AD(M-m)/M\sqrt{2}$, where A is the area, D the density of the oxide, M its molecular weight and m the weight of metal in M of oxide.

The integrals

$$k_7\int_0^\infty t^{-1/2}e^{-k_5t}dt \quad \text{and}$$

$$k_7\int_0^\infty t^{-1/2}e^{-k_6t^3}dt$$

are both *finite*, so that (in contrast with the Tunnel Effect mechanism) a *truly asymptotic* curve may be expected. The values of the integrals are $k_7\Gamma(\frac{1}{2})/k_5^{1/2}$ and $k_7\Gamma(1/6)/3k_6^{1/6}$ respectively, and clearly the final thickness will be affected by changes in the constant (k_7) governing the parabolic thickening and hence by temperature. Price and Thomas[55] have shown that the constant k_4 (and hence k_7) is *extremely* susceptible to impurities in the film, and it is not surprising to find that the final weight increase reached by Vernon's specimen A (purity 99.98%) should be lower than that reached by B (purity 99.61%).

The formation of internal cracks parallel to the surface does not eliminate stresses completely, and when cracks starting at different nuclei (not necessarily at the same level) approach one another, a situation arises in which the catastrophic (flaking) form of breakdown may be expected. When once this starts at a point, it is likely to extend over the greater part of the surface, and as this form of breakdown must admit oxygen to the metal at the base of the film, the whole process can then start again. Vernon's weight-time curves show this sudden explosive rise every few weeks. Apparently the film remains adherent at some points (otherwise there would be *loss* of weight), and if so, less than 100% of the area must be available for renewed oxidation. It is to be expected that the increase of weight experienced during the period between the first and second catastrophes should be less than that experienced before the first, and the subsequent increases smaller still. Vernon's curves show this to be the case.

The mechanism of delayed cracking accounts for the main features of Vernon's curves, but Dr. Vernon has himself suggested that attempts at curve fitting would not be justified, since the experiments, designed for another purpose, were not carried out under conditions of constant temperature, humidity and atmospheric pollution. When long-period curves carried out at constant temperature become available, it should be possible to obtain further information by ascertaining whether the various equations set down above (or others which may be developed to represent other cases) fit the experimental data.

My thanks are due to Prof. N. F. Mott, Dr. W. H. J. Vernon, Dr. T. P. Hoar, Dr. J. N. Agar, Dr. D. H. Bangham, and Mr. A. U. Huddle for many fruitful ideas and much salutary criticism, and particularly to Dr. E. Orowan for a suggestion which provided the key to the situation, and to Dr. A. J. Gould who, in addition to other help, drew the diagrams.

Summary of Conclusions

Outward migration of cations and electrons by means of lattice defects normally gives parabolic thickening ($dy/dt = k_4/y$) except in the early

stages; k_4 depends on the electrical constants of the film-substance. If mechanical breakdown occurs in the film, which is normally in lateral compression, other laws may come to be obeyed. There is experimental evidence of the compressional stresses and of the breakdown. Breakdowns may be of three kinds: the relation between adhesion, cohesion and compressional energy should decide which of the three will occur:

(1) *Blistering* should occur where adhesion is poor and cohesion high. It should lead to *rectilinear thickening* ($dy/dt = k_1$) if the cracks in the blister-wall admit oxygen to the cavities, so that new oxidation starts at the base of each blister, but otherwise to *logarithmic thickening*, since the outward movement of cations, although aided by wall-migration along rifts normal to the surface, is interrupted by cavity barriers parallel to the surface. The chance that a given point can escape being covered by such a barrier is proportional to $e^{-k_3 y}$, giving $dy/dt = k_2 e^{-k_3 y}$.

(2) *Flaking* over big areas should be rare but catastrophic, leading to resumption of oxidation at roughly its original high rate.

(3) *Shear-cracking* should occur where adhesion is high and cohesion low, and should generally lead to rectilinear or parabolic thickening or to intermediate forms.

The theory developed has been applied to interpret the experimental results of Vernon, Miley and others, and particularly explains the remarkable fact that conditions prevailing at the outset of exposure dictate subsequent behavior—even when conditions change; the obedience to a simple law under fluctuating conditions has hitherto been difficult to understand. The probable relationships between k_1, k_2 and k_4, the main velocity constants of the three laws, have been explored, and the results may prove helpful in interpreting future work.

References

1. W. H. J. Vernon, Trans. Faraday Soc. **19,** 839 (1923); **23,** 113 (1937).
2. W. H. J. Vernon, Trans. Faraday Soc. **27,** 255 (1931).
3. W. H. J. Vernon, Trans. Faraday Soc. **31,** 1668 (1935).
4. N. B. Pilling and R. E. Bedworth, J. Inst. Met. **29,** 529 (1923).
5. J. S. Dunn, Proc. Roy. Soc. (A) **111,** 203, 210 (1926).
6. W. Feitknecht, Z. Elektrochem. **35,** 142 (1929); **36,** 16 (1930).
7. F. J. Wilkins and E. K. Rideal, Proc. Roy. Soc. (A) **128,** 394, 407 (1930).
8. A. Portevin, E. Prétet and H. Jolivet, Rev. Met. **31,** 101, 186, 219 (1934). J. Iron Steel Inst. **130,** 219 (1934).
9. W. H. J. Vernon, E. I. Akeroyd and E. G. Stroud, J. Inst. Met. **65,** 301 (1939).
10. A. B. Winterbottom, Trans. Electrochem. Soc. **76,** 327 (1939).
11. A. L. Dighton and H. A. Miley, Trans. Electrochem. Soc. **81,** 321 (1942).
12. J. Bénard and O. Coquelle, Compt. rend. **222,** 796, 884 (1946).
13. B. Lustman, Trans. Electrochem. Soc. **81,** 359 (1942).
14. C. Wagner and K. Grünewald, Z. Phys. Chem. (B) **40,** 455 (1938).
15. D. H. Bangham, J. Sci. Inst. **22,** 230 (1945), quoting V. Bloomer.
16. L. B. Pfeil, J. Iron Steel Inst. **119,** 501 (1929); **123,** 237 (1931).
17. C. Wagner, Z. Phys. Chem. (B) **21,** 25 (1933); Trans. Faraday Soc. **34,** 851 (1938).
18. T. P. Hoar and L. E. Price, Trans. Faraday Soc. **34,** 867 (1938).
19. L. E. Price, Chem. Ind. **1937,** p. 769.
20. U. R. Evans, Trans. Electrochem. Soc. **46,** 247 (1924).
21. K. Fischbeck, Z. Elektrochem. **40,** 522 (1934).

22. U. R. Evans and L. C. Bannister, Proc. Roy. Soc. (A) **125,** 370 (1929).
23. R. T. Phelps, E. A. Gulbransen and J. W. Hickman, Ind. Eng. Chem. (Anal.) **18,** 391 (1946).
24. N. F. Mott, J. Inst. Met. 1926 (May lecture).
25. U. R. Evans, Trans. Faraday Soc. **41,** 365 (1945).
26. W. S. Patterson, J. Soc. Chem. Ind. **49,** 203T (1930).
27. U. R. Evans, J. Inst. Met. **65,** 330 (1939).
28. U. R. Evans, Trans. Electrochem. Soc. **83,** 337 (1943).
29. U. R. Evans, J. Inst. Met. 1945.
30. E. Orowan, Z. Physik **82,** 253 (1933).
31. U. R. Evans, J. Chem. Soc. **1927,** p. 1020.
32. S. C. Britton and U. R. Evans, J. Chem. Soc. **1930,** p. 1773.
33. U. R. Evans, Nature **157,** 732 (1946).
34. U. R. Evans and J. Stockdale, J. Chem. Soc. **1929,** p. 2651.
35. G. I. Finch and A. G. Quarrell, Proc. Roy. Soc. (A) **141,** 398 (1933); Proc. Phys. Soc. **46,** 148 (1934).
36. M. Straumanis, Z. Phys. Chem. (B) **19,** 63 (1932).
37. J. S. Anderson and J. R. Richards, J. Chem. Soc. **1946,** p. 537.
38. F. N. Rhines and others, Amer. Inst. Min. Met. Eng. Tech. Pub. **1162** (1940), **1368** (1941), **1439** (1942), **1617** (1943), **1645** (1943).
39. C. S. Smith, J. Inst. Met. **46,** 49 (1931).
40. P. A. Jacquet, "Sur un nouveau réactif micrographique du cuivre et ses applications" (Compagnie Générale de Constructions Téléphoniques. Notice VII).
41. R. Griffiths, J. Iron Steel Inst. **130,** 380 (1934).
42. U. R. Evans, Kolloid Z. **69,** 129 (1934).
43. A. Nadai, "Plasticity," Chapter 17, McGraw-Hill (1931).
44. A. A. Taylor and J. W. Cobb, Trans. Inst. Gas. Eng. **88** 106 (1938-39).
45. G. Hägg and J. Sucksdorff, Z. Physik, Chem. (B) **22,** 444 (1933).
46. L. L. Bircumshaw and M. H. Everdell, J. Chem. Soc. **1942,** p. 598.
47. J. S. Dunn and F. J. Wilkins, "Review of Oxidation and Scaling on Heated Solid Metals" 1935, Section IV (Department of Scientific and Industrial Research).
48. E. A. Gulbransen, Trans. Electrochem. Soc. **87,** 589 (1945).
49. T. E. Leontis and F. N. Rhines, Amer. Inst. Min. Met. Eng. Tech. Pub. **2003** (1946).
50. J. C. Warner, Trans. Electrochem. Soc. **83,** 319 (1943).
51. W. Feitknecht and R. Petermann, Korrosion und Metallschutz **19,** 181 (1943). W. Feitknecht and H. Weidmann, Helvetica Chimica Acta, pp. 1560, 1911 (1943).
52. F. A. Champion, Trans. Faraday Soc. **41,** 593 (1945).
53. N. F. Mott, Trans. Faraday Soc. **35,** 1175 (1939); **36,** 472 (1940); J. Inst. Met. **65,** 333 (1939).
54. J. Frenkel, Phys. Rev. **36,** 1604 (1930).
55. L. E. Price and G. J. Thomas, J. Inst. Met. **63,** 21, 29 (1938).

Plastics for Corrosion Control ★

*By J. W. Shackleton**

THIS ARTICLE is concerned with the practical aspects of the application of some recently developed plastics to the prevention of corrosion or, more particularly, chemical attack. The subject of corrosion-resistant coatings is broad, and comments are limited primarily to materials with which readers may not be familiar.

The problem of corrosion, of course, may be attacked in a number of ways. Anti-electrolysis procedures are the subjects of current, wide discussions. Corrosion-resistant alloys answer many needs, as do surface treatments such as electroplating. There are many types of protective coatings in use, both organic and inorganic.

Organic coatings can be divided into various groups, depending upon the outlook of the investigator. Paints, lacquers, and enamels are well known. These are film-formers with or without pigments or other additives, which can be applied by spraying or with a brush. There are a number of resinous coatings which are of interest, including plastics or rubber which can be applied from solution, or by other means, and then cured. Many problems of corrosion are solved by the application of rubber sheeting, or a synthetic rubber such as neoprene applied as sheet or as a "troweled-on" coating.

For purposes of record, the low-pressure laminating materials, which are principally polyesters, are mentioned. This is a new group of plastics with unusual properties. Generally, they have excellent abrasion-resistance and their chemical properties may be of interest in corrosion control. However, they are not as yet sufficiently developed as coating materials to warrant discussion at this time.

With various types of materials available, those persons unfamiliar with the situation might think that little remains of the problem of combating corrosion. However, that there are many corrosion problems remaining is attested by the great number of inquiries we receive daily for materials which will give better service, or which will meet a specific need.

Apparently, from comments received, there is a great lack of familiarity with the newer plastics, especially those in the category of thermoplastics. The difference between thermoplastics and thermosetting resins is in the matter of heat curing. Phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde and the new polyesters, so-called low-pressure resins, are thermosetting in nature; that is, they are vulcanized by heat. The thermoplastics, on the other hand, are not permanently hardened by heat.

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Cellulosic Plastics

One of the earliest applications of thermoplastics in corrosion-resistance was the wrapping of pipe which was to be laid in acid or alkaline soils, with cellulose nitrate sheeting. A great deal of this type of coating was carried out, and it is understood that the wrappings gave excellent service in many cases. Cellulose acetate and ethyl cellulose have been used as a corrosion barrier in a limited number of applications, but the chemical resistance of these materials is not outstanding and the uses are thereby limited.

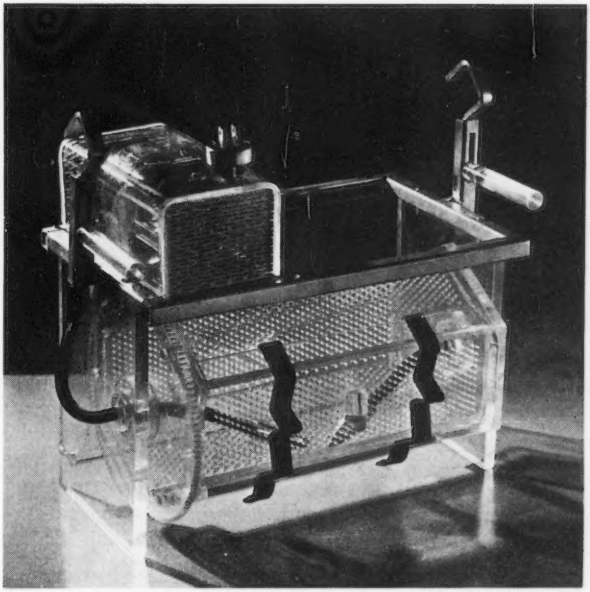

Figure 1—A plating barrel of Lucite, acrylic resin, which has no obstructing ribs or crevices common to the old type barrel, and permits free movement of the parts during plating and ready unloading of finished parts. The plastic provides the added advantages of inertness to chemical solutions, increased durability, lighter weight, and lower electrical conductivity.

Polyvinyl Alcohol

Polyvinyl alcohol has remarkable resistance to organic solvents. Wire baskets have been coated with polyvinyl alcohol and then used in carbon tetrachloride and other degreasing agents with good results. Tanks coated with polyvinyl alcohol are used for the storage of chlorinated hydrocarbons and other organic solvents. Unfortunately, polyvinyl alcohol is soluble in water and its applications are therefore limited.

Acrylic Resin

An acrylic resin, Lucite, in fabricated form has been used by the electroplating industry for corrosion control. This plastic has been used for insulators in various parts of electroplating tanks; for example, installed behind anodes, it is said to prevent plating on the wall of the tank. It is a rigid thermoplastic and is easily shaped and machined. It is light in weight, has good impact-resistance, does not become brittle at low temperatures, and is not affected by sudden changes of temperature. Plating barrels made from this material permit higher current densities, and consequently higher rates of production (Figure 1).

This acrylic resin is resistant to

chromium, cadmium, nickel, silver or other plating solutions at temperatures up to 140° F. In one installation, it has been used more than two years in high-caustic zinc solutions. One 28,000-gallon anodizing tank has been successfully lined with sheets of "Lucite." The plastic is easily repaired with commercially available cements and long service can be expected.

Films of acrylic resins and their copolymers have been produced, and their chemical and physical properties indicate a limited utility for corrosion-control.

Vinylidene Chloride

Vinylidene chloride resins, generally known by the trade name Saran, are produced by The Dow Chemical Company. Pipe made from it has been useful in various chemical plants. Vinylidene chloride resins can be made in the form of emulsions and are useful coating materials. However, the applications involving their use on metal are limited by the fact that slight instability produces hydrogen chloride gas, which itself may attack the metal.

Vinyl Chloride Resins

Vinyl chloride resins have been used in various forms as coatings, but more recently methods have been devised for dispersing them in organic media. Coatings applied through the use of these dispersions are generally fused into continuous films at a temperature of about 350° F. The dispersions are known as plastisols or organisols depending upon the plasticizer and solvent content.

These materials have good chemical resistance and are widely used in the electroplating industry. Although they are probably not as resistant to attack by chemicals as is the vinylidene chloride plastic, they are somewhat more stable and easier to apply.

Nylon

A series of polyamide resins with unusual properties is designated by the generic name nylon. The nylons are tough, abrasion-resistant polymers with excellent chemical resistance. Although they are thermoplastic in nature, their heat-resistance is generally higher than that of other resins of this class. For example, nylon (molding type) is form-stable at temperatures to 400° F., although gradual increase in flexibility may limit it to service temperatures below 300° F. It retains good impact strength at sub-zero temperatures.

The nylon resins are attacked by mineral acids, but they have excellent resistance to most organic solvents, including hydrocarbons and chlorinated hydrocarbons. The only true solvents for most nylons are phenols, cresols, and certain other organic compounds of this type. The resistance of nylon to hot, strong alakli is very good.

Several specially prepared members of the nylon family are soluble in mixtures of alcohol and water. Thus solutions may be produced which can be used for coating. The resistance of such coatings to gasoline and many other solvents is excellent. Cresylic acid solutions of nylons have been used commercially for coating. Unfortunately, the most chemically resistant forms of nylon are not generally recommended for

coatings or the production of films. The "soluble" types, which have been employed most extensively as coating materials, are to a certain extent water-sensitive and some chemical resistance has been sacrificed in the attainment of modifications which can be dissolved in alcohol-water mixtures and deposited from solution.

Although nylons will not be useful in the presence of acids, there are numerous possible applications for them in the lining or coating of chemical equipment. One interesting example is the use of a nylon for the lining of aviation fuel cells. Many gasketing applications are being studied.

Polythene and Teflon

There are two new plastics which warrant extensive consideration by engineers interested in problems of corrosion. These two plastics are polythene and polytetrafluoroethylene. The latter is known as "Teflon."

Polythene is a generic name for polyethylene, the solid polymer produced from ethylene gas under carefully controlled conditions. The polymer is produced as a white powder which, can be used as such or screened to 60-mesh fineness.

This white powder may be compacted and then recut to a proper granular size for molding or extrusion; from this granular form can

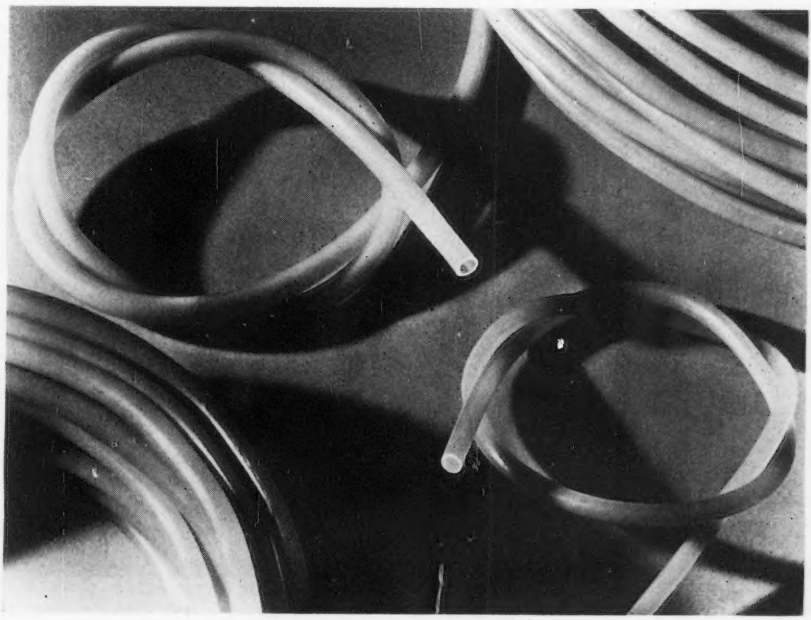

Figure 2—Polythene tubing.

be produced a wide variety of shapes, for example, sheets, rods, tubes and custom-designed articles. (Figure 2).

A number of methods for coating surfaces with polythene have been developed and some of these are worthy of refinement to commercial processes. Thin coatings can be produced from solutions of polythene in hot solvents such as chlorinated hydrocarbons. The solutions must be used hot to prevent their gelling. Of course, on a commercial basis this would entail solvent-recovery which is generally troublesome and expensive.

Flame-Spraying

A great deal of work has been done on the flame-spraying of polythene, in which the 60-mesh powder is applied by means of a flame-pistol Unfortunately, these flame-guns were developed for the spraying of powdered metals and the temperatures of the flame tend to degrade plastics, which have lower heat-resistance. The flame-spray process as applied to plastics has inherent disadvantages, for example, cost of application, difficulty in obtaining requisite adhesion and inability to produce coating which duplicate the characteristics of the polymer in sheet form. Other devices for coating with powder have been studied and each of these has limited potential applications.

Our laboratories for some time have had in the process of development a method for coating tanks with polythene sheeting. This development work has not progressed to a point permiting discussion, but it is safe to predict that a method for coating chemical tanks, tanks for storage of food and water, still columns, centrifuge barrels, ducts, exhaust systems and so forth, with polythene sheeting will be the result of present investigations.

Consider for a moment the properties of polythene which make it of special interest in the field of corrosion-control. Polythene will be a relatively low-priced plastic used in large volume, not only in this industry but also for packages, containers and closures and as a dielectric for wire and cable, especially in high-frequency applications.

Only a very few chemicals have any noticeable effect on polythene. The only common solvents which affect it at all are chlorinated hydrocarbons and certain of the parent hydrocarbons. These swell the plastic if they are in contact for a long time. Polythene is resistant to oils and greases, but may be swelled somewhat by them on long exposure.

Polythene will absorb free halogens, but even so it is being studied for some applications with these materials, since the attack is not severe.

Resistance of Polythene

Polythene is not attacked by concentrated mineral acids, including hydrofluoric acid, nor by caustic solutions. It is particularly resistant to inorganic chemicals of all kinds. It has remarkable resistance to oxidizing and reducing agents. Concentrated nitric or sulfuric acid at 200° F. will oxidize and char the plastic. Acetic acid does not attack it, but films of polythene are reported to be permeable to acetic acid and we are not certain that it will protect metals from this corro-

sive agent. Further studies on permeability are being carried on at present.

In addition to its chemical resistance polythene is unusual in its wide variety of excellent properties. It has a specific gravity of 0.92. Its water-absorption is negligible and few materials show moisture-vapor-transmission rates as low as those of polythene. It is completely ordorless, tasteless, and nontoxic. Even in the absence of plasticizer, polythene is flexible to temperatures below -70° F. This lack of need of a plasticizer is advantageous since plasticizers are often troublesome, especially in films of plastic, through leaching out, exuding or evaporating, to leave a hard and embrittled coating, or to contaminate solutions with which they come in contact.

Polythene has extremely high impact strength, its electrical properties are outstanding and a potentially low price is indicated.

Among recent developments in plastics, the discovery of polymers of tetrafluoroethylene, "Teflon," has been outstanding. This unique plastic is finding many applications as gaskets, packing, linings, fittings, pipes, etc., where extreme corrosion-resistance is required. (Figure 3).

The potential value of Teflon to corrosion control becomes apparent when it is realized that the only

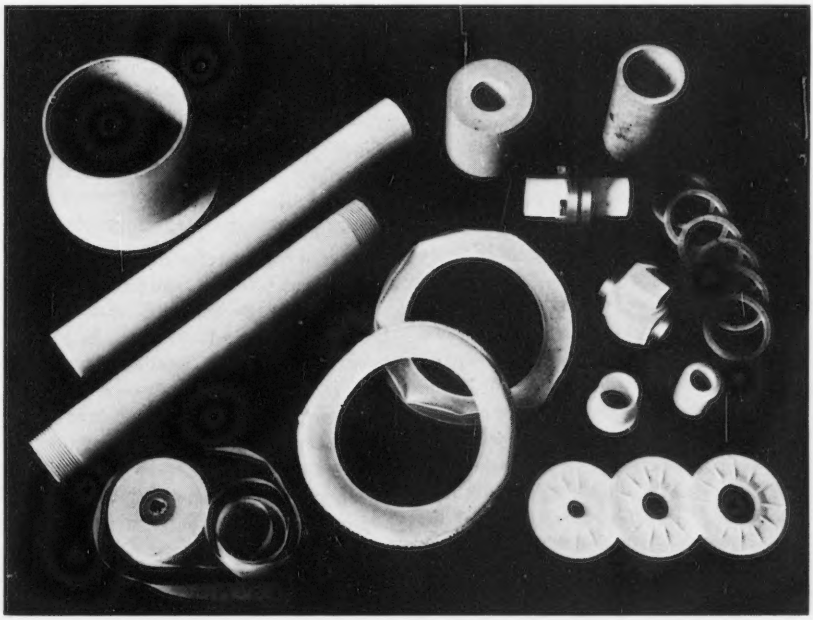

Figure 3—Tetrafluoroethylene resin is displayed as flared tubing, threaded pipe, cylinders, coaxial cable spacers, gaskets, tape, a plug cock, a valve-stem packing, and a rod. It has great heat endurance, unusual resistance to solvents and corrosive agents, and good insulation for high frequency currents.

chemicals known to attack it are molten alkali metals and free fluorine gas at 300° F. Concentrated sulfuric acid at 300° C., hydrogen fluoride at 100° C., nitric acid at 85° C., fuming nitric acid and sulfuric acid and aqua regia have no effect on this material. Chlorosulfonic acid BF_3-HF (boron fluoride-hydrogen fluoride mixture), various peroxides, and fused sodium hydroxide at 300° C. have no corrosive action whatever on this remarkable material. Organic reagents do not harm it. Hydrocarbons of all types, chlorinated hydrocarbons, phenols and cresols, formic acid, nitro compounds and many others were tested without finding one which would even slightly swell the polymer. Teflon was boiled with dibutyl phthalate without detriment. The water-absorption in the ASMT test (D570-42) is zero.

This material has a service temperature range from -70° to 550° F. At the lower temperature, the polymer is still tough and flexible. Heated for one month at 300° C., test bars showed a decrease of only 10 to 20 percent in tensile strength. Electrical properties are likewise unusual. The power factor is 0.0002 at all frequencies measured, up to 3×10^9 cycles, and, over the same frequency range, the dielectric constant is 20.

The impact strength is high and the tensile strength and other mechanical properties are adequate for a wide number of uses. Teflon when used as a gasket will form a satisfactory seal by virtue of limited flow properties.

Inert fillers can be incorporated in Teflon prior to fabrication to alter its properties. Graphite may be added to soften the plastic and make it flow more easily. A corrosion-proof, molded packing ring composed of 93 percent of Teflon, the remainder being graphite and a bonding agent has been developed. Its applications include packing on rotary shafts, pumps, agitators, valves and gaskets.

Ground mica may be mixed with it to produce more rigid moldings, and other fillers of interest are being studied.

Unfortunately, the very advantages which give Teflon its position among plastics make difficult its fabrication into useful articles. Ordinary techniques of molding and extrusion are not applicable to this polymer. The plastic can be extruded in the form of rods and tubes or as an insulation on wire, but rates of production are very slow. Compression moldings of simple design can be made by special techniques. Sheets and films can be produced by shaving baked cylinders or blocks.

Because of the extraordinary chemical inertness of this plastic, no cement has yet been found which will adhere to it. This quality can be used to advantage, however, where a surface is needed which will facilitate the release of agglomerating or tacky substances that give trouble by building up on other materials.

The lack of solvents for Teflon also precludes the hope of making coating solutions with the material. A method of depositing coatings from aqueous suspensoids is in the preliminary research stages.

The material machines well with standard tools.

Testing and Selection of Inhibitors for Corrosive High Pressure Condensate Wells

By D. A. Shock*

THE MOST EFFECTIVE method of combating high pressure condensate well corrosion yet found is in the use of some inhibitor. The experience of the industry, since the reporting of this type of corrosion,[1] has shown that thus far no single inhibitor has been proved applicable to all condensate fields. The purpose of this paper is to review the methods thus far devised for testing inhibitors, the requirements which should be met by a satisfactory inhibitor, and to give a discussion which may aid in the search for new inhibitors.

Evaluation of Corrosiveness

In order to evaluate fully the effect of an inhibitor, it is necessary to evaluate the original corrosiveness in the well. Visual inspection and records of abnormal replacement of tubing and fittings indicate a corrosive condition beyond question. Tubing calipering[2] is now used extensively to show corrosion in the wells, and other indirect methods such as Penetron[3, 4] show interior surface corrosion. These indirect methods have their limitations and require expert interpretation. The corrosion evaluation gained is too slow to be used in primary inhibitor evaluation. Such methods are useful over long time periods to prove the inhibitor is satisfactory for field use, but not of much value for testing purposes.

The most useful methods now employed for corrosion and inhibitor evaluation in the wells is obtained by the change in ppm of iron in the produced water after injection, and the change in the effect of the produced gas and fluid on a mild steel coupon exposed in the well.

A thorough discussion of these methods cannot be made here, and exact interpretation as to the degree of corrosion in a well shown by these methods is still not well established; however, for purposes of evaluation of an inhibitor, there are some generalizations which seem to hold true. First, a high iron content in the produced water, 200-300 ppm, generally shows a corrosive condition.[5, 6] Since it has been shown that this is not always the case,[7] the corrosive condition of the well should be verified by some other means, e.g., replacement and visual inspection.

A drop in iron content on introduction of inhibitor in a corrosive well is generally taken as indicating reduction in the corrosive condi-

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tion, and the effectiveness of the inhibitor is sometimes reported as the percent drop in iron content. The second main method of evaluating corrosion is based on coupon behavior, and has been applied with a number of variations.[7, 8, 9, 10] The work thus far indicates that, after descaling the coupon and calculating the loss in weight over the exposed area of the coupon to a value expressed as inches penetration per year, if the value is over 0.005 after a two-week exposure, a corrosive condition exists. A serious corrosive condition is believed to exist if the value is 0.010 or over.

The effect of the inhibitor is taken by the reduction in rate of attack. A protection value is sometimes given from the change in the inches penetration per year value, e.g., a drop from 0.010 to 0.000 inches penetration per year is 100 percent protection, which is ideal; a drop from 0.010 to 0.005 would be 50 percent protection, which is not enough reduction to indicate a good inhibitor on this basis alone.

Methods of Inhibitor Injection

After the corrosive character of the well is established and evaluated, there is the question of method of inhibitor injection. Three systems have been tried, although only one has found wide use. The nature of the inhibitor will depend somewhat on the method of treatment. The methods are as follows:

1) Injection down the casing or auxiliary casing, and return through the tubing.
2) Injection through macaroni tubing inserted in the flowing tubing.
3) Solution of a solid plug which has been lubricated and dropped into the tubing.

The first method is in common usage and necessitates a means of introducing the inhibitor into the well. Apparatus for this operation has been described in several papers.[11, 12, 13, 14, 15, 16] High pressure pumps driven either by gas expansion or by gasoline engines or electric motors, and gas pressure lubricators are the usual systems employed.

An inhibitor which requires only a small amount of injection per day, is soluble in hydrocarbon, and does not salt out or freeze in the pump or injection lines, is to be desired. Of course, the efficiency of an inhibitor may offset any mechanical disadvantages; however, the above factors should be kept in mind as mechanical requirements if the inhibitor is to be used in the liquid form.

No data is available on the operation of macaroni tubing for inhibitor injection; this is in the experimental stage and is mentioned here because of its possible importance. The same mechanisms for injection would be necessary as for the previous category and the same features would be desirable in an inhibitor for use in this injection system.

Use of solid plugs for chromate injection has been reported[17] by the Bureau of Mines, and the apparatus described. This method of injection has very definite advantages from a servicing and operational standpoint, if it can be made to provide adequate inhibition. The requirement that the inhibitor be solid limits the possible inhibitors now

available. Incorporation of the inhibiting substance with a slowly soluble solid which could be injected by this means should receive consideration. The examination of possible inhibiting compounds should be a valuable starting point in formulating a solid injection inhibitor.

Regardless of the method of injection, it is highly important that some system of check be made on the return of the inhibitor after injection. That is, there should be some means of knowing whether or not the inhibitor is getting into the well and returning up the tubing.

Furthermore, it is important to have some quantative data on the amount of inhibitor returned. The inclusion of eosin, fluorescein, or an oil soluble dye in the injected inhibitor has been proposed to follow the return concentration. Since such dyes have been found to have inhibiting value against acid attack,[18] the addition of these traceable compounds to other inhibitors seems practicable. Analysis for the inhibitor itself seems best if possible; however, for most of the proprietary inhibitors such analysis is not feasible.

Data Necessary for Field Evaluation

From the experience gained by inhibitor injection in a number of fields it has become obvious that it is desirable to take certain data during the test period. While it is impracticable and sometimes impossible to obtain all of this data, the following outline gives the points believed to be of value:

1) The normal corrosion value of the well, preferable iron in produced water and inches penetration per year value on a steel coupon.
2) Well data, e.g., depth, pressure, average flow, average temperature, gas to liquid hydrocarbon ratio, liquid hydrocarbon to water ratio or measure of produced water. Physical operation should be held as near constant as possible while well is under test.
3) Analytical data: carbon dioxide in gas, hydrogen sulfide in gas, water analysis, organic acids, calcium and magnesium, chloride, sulfate, total solids.
4) Introduce inhibitor by some means such that the rate of injection can be controlled or known. If possible, the amount and rate of return up the well.
5) Measure the change in corrosion rate by running tests. Various exposures of coupons to get inches penetration per year values; various analyses of water to get iron value while under inhibition.
6) Stop inhibitor injection to see if corrosion rate comes back to established value and check to see if there has been a change in well corrosive condition during the time the well was under test.
7) Vary the rate of inhibitor addition and note variation in corrosive rate. Try to establish minimum safe injection rate.
8) Keep records of flow, pressure, rate of production throughout the test so that any tendency for restriction or plugging is shown.
9) Note any effect that inhibition method has on plant operation, e.g., odor, emulsifying power, etc.

Running records such as are taken by the Bureau of Mines[11] and recorded by graphical means and field test such as reported in West Tuleta Field[19] show the application of these principles.

Laboratory Inhibitor Tests

At the present time no laboratory selection or testing method has been reported which simulates field conditions well enough to give reasonable assurance that the laboratory results would be indicative of field experience. Three classes of laboratory approaches to inhibitor evaluation have been reported; they are:

1) Coupon exposure tests with corrodent, measured against change in inches penetrated per year.
2) Coupon tests measured against wetting ratios.
3) Photomicrographic study of film in corroding and inhibited systems.

The first method class has been applied to coupons exposed both at atmospheric and high pressure to the recognized corrodent, carbon dioxide and fatty acids, as well as naturally occurring corrosive waters and produced liquid hydrocarbons. C. K. Eilerts[11] shows the effect of use of sodium chromate against the corrosive attack of carbon dioxide, fatty acids, and phenol by this method. A number of proprietary inhibitors have been tested by Battelle Memorial Institute for the NGAA Corrosion Research Project Committee by using the water and liquid hydrocarbon from a well known to be corrosive and comparing the inches penetration per year values after addition of an inhibitor. A number of promising inhibitors were thus indicated. This method also gave results which showed the tendency of some inhibitors to accelerate corrosion when its concentration was below certain values even though the higher concentrations afforded protection. The method, therefore, has been used with some success to predict compounds which would be of value as inhibitors.

The second method is reported by Rogers,[20] and consists of relating the inhibiting powers to the preferential wetting of steel when exposed to well water and condensate at atmospheric pressure when condensate, water and inhibitor concentrations are varied. This method affords a more direct approach to protecting against the corrosiveness of the fluids of the well. Results from these tests have been valuable in showing that the variation in water to liquid hydrocarbon can change the corrosive character of the well and the ranges of inhibitor concentration necessary to give preferential wetting.

The third method attempts to study the formation of protective films which result from additions of possible inhibiting substances to the water or hydrocarbon. Napthenic acid and sodium chromate have been shown[21] to yield such protective layers. It is expected that this type of information will give a more scientific basis on which inhibitors can be selected.

Selection of an Inhibitor

Operating Requirements

Taking into consideration that most inhibitor treatment requires that the inhibitor be injected, the following qualities are to be sought

in an ideal inhibitor for injection:

1) Effective in all types of wells.
2) Safe—concentration changes do not accelerate corrosion or cause pitting.
3) Require a small volume and be easy to inject (no freezing or plugging).
4) Cause no difficulty in operation (no well plugging or smell of product or emulsion difficulties).
5) Economical.
6) Traceable.

Practical Results

It is recognized that an inhibitor may function satisfactorily in a field without meeting a number of these points. The use of sodium dichromate, Kontol 115, ammonia and soda ash have been reported to be successful for specific fields or wells; however, with the exception of Kontol 115, each of these have proved that the inhibitor could not be used in all fields. An inhibitor which functions more like the natural inhibiting substances believed present in some fields and wells is being sought. The naphthenic acids were advanced as possibly being the inhibiting substance; however, field work shows that, although corrosion is reduced in all cases, injection of naphthenic acid does not totally inhibit corrosion in some cases. It is believed that when the polar compounds contained in the hydrocarbon of non-corrosive, naturally inhibited wells can be identified, an insight will be gained as to the class of compounds to which these substances may belong. Progress is being made on this method of attack by the NGAA Corrosion Research Project Committee by adsorbing the polar compounds from the hydrocarbon on silica gel to concentrate these compounds. The saturated gel is then to be desorbed and an effort made to separate and identify the adsorbed compounds.[22] It is expected that the active agents in these compounds would fit most of the requirements of a good injection inhibitor.

Types of Compounds Which May Be Expected to Act as Inhibitors for High Pressure Condensate Wells

While the exact mechanism of high pressure well corrosion is not generally agreed upon, it is generally conceded that the corrosion is due to an acid attack, either carbonic, fatty acid or both. Thus, it is reasonable to assume that acid inhibitors should be used to combat the corrosion. From the theoretical and practical knowledge accumulated, the following general types of compounds may be expected to find use as inhibitors:

1) Compounds which adjust the pH to a high enough value so that the iron is not attacked. Neutralization with sodium hydroxide or other base accomplishes this. This method has had field test but has the disadvantage of plugging wells which precipitate solids before protective pH is obtained. Ammonia addition may partially function this way and is more successful than the sodium bases. A buffer which would bring the pH to a protective value and still keep the solids in suspension could conceivably act as an inhibitor. There is evidence that this is the case

in certain wells which produce a high borate water.[23]

2) Compounds which adsorb to the surface of the steel and prevent acid type attack. Many of the proprietary inhibitors, complex amines, bone oil, etc., operate in this manner. Complex molecules containing one or more polar groups are known to act in this manner. Since the same type of compound may behave as following categories 3 and 4, it is difficult to say which is the controlling protective mechanism for many of these substances.

3) Differential wetting and emulsification power. Since water is required for the corrosion to take place, it is believed that a continuous film of oil over the steel (no water wetting) would inhibit corrosion.

4) Protective coating by corrosion product—the protective coat on the naturally inhibited well[21] seems to be of this category. The corrosion surface is too thick to be considered physical adsorption only. Also, there is evidence of compound formation which is a chemical, not a physical, film. For this type of compound it would seem necessary that it be acidic enough to unite with iron and form an insoluble iron compound which would tend to form an impervious, adherent, coherent film.

Acknowledgment

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References

1. Bacon, T. S., and Brown, E. A., Corrosion in Distillate Wells. Pet. Eng., **14,** 10, 131-2 (1943).
2. Chaney, P. E., Internal Tubing Caliper Measures Extent and Location of Corrosion, Oil & Gas J., **44,** 50, 115 (1946).
3. Penetron Quickly Determines Steel Thickness, Oil & Gas J., **44,** 8, 106 (1946).
4. Radiographic Inspection of Oil Field Equipment in Place a Convenient Tool, Oil & Gas J., **43,** 29, 91 (1944).
5. Bacon, T. S., Investigation and Control of Condensate Well Corrosion, NGAA Corrosion Research Project Committee Minutes, Aug., 1945 50-1.
6. Griffin, H. T., and Greco, E. C., Laboratory Studies for Determination of Organic Acids as Related to Internal Corrosion of High Pressure Condensate Wells, Corrosion, **2,** 138, (1946) Sept.
7. Bacon, T. S., Corrosion in the Opelika Texas Field, NGAA Corrosion Research Project Committee Minutes, **3,** 150, Oct., 1946.
8. Bacon, T. S., Wellhead Coupon Exposure Testing, NGAA Corrosion Research Project Committee Minutes, **2,** 15-20, Nov., 1945; Ibid. **2,** 41-9, Aug., 1945.
9. Hackerman, Norman and Shock, D. A., Nature of Surface Layers Formed on Steel in High Pressure Gas Condensate Wells, Ind. & Eng. Chem., In Press.
10. Shock, D. A., NGAA Well Coupon Survey, NGAA Corrosion Research Project Committee Minutes, **3,** 102, (1946) Oct.
11. Eilerts, C. K., Carlson, H. A., Smith, R. V., Archer, F. G., and Barr, V. L., Use of Sodium Chromate as a Corrosion Control Medium in Gas Condensate Wells, Oil & Gas J., **45,** 124, May 18, 1946; Corrosion, **3,** 73 (1947).

12. Buchan, R. C., Corrosion and Preventive Methods in the Katy Field, API, 26th Ann. Mtg., Chicago, Ill., Nov. 13, 1946.
13. Bacon, T. S., Chemical Treatment of Distillate Wells—Practical Aspects, Corrosion, **2,** 188, (1946) Oct.
14. Menaul, P. L., Investigation and Control of Condensate Well Corrosion, Corrosion, **2,** 195, 1946 (Oct.).
15. Yale, W. D., Prevention of Condensate Well Corrosion by Chemical Treatment in the Erath Field, Corrosion, **2,** 85 (1946) Mar.
16. Hock, R. L., Corrosion in High Pressure Distillate Wells, NGAA Corrosion Research Project Committee Minutes, **3,** 184, (1946) Oct.
17. Eilerts, C. K., Treatment of a Gas Condensate Well Subject to Corrosion with Solid Sticks of Sodium Chromate Injected into the Tubing Against the Flow of Fluid, NGAA Corrosion Research Project Committee Minutes, **3,** 97, (1946) Mar.
18. Ardagh, E. G. R., and Roome, R. M. B., and Owens, H. W., Mechanism of Corrosion of Iron in Sodium Chloride Solution, Ind. & Eng. Chem., **25,** 1116 (1933).
19. Justice, W. H., and Jones, E. N., Tests at Cycling Project Demonstrate Possibilities of New Corrosion Inhibitor Kontol 115, Oil & Gas J., **45,** 86-7, N 9 (1946).
20. Rogers, Walter F., and Waldrip, H. E., Results of Some Studies of the Condensate Well Corrosion Problem, Corrosion, **3,** 121 (1947) Mar.
21. Shock, D. A., and Hackerman, Norman, Corrosion Studies in Natural Gas Condensate Wells II—Protective Layers, Ind. & Eng. Chem., In Press.
22. Shock, D. A., Activity Report to NGAA Corrosion Research Project Committee, NGAA Corrosion Research Project Committee Minutes, **3,** 104 (1947).
23. Carlson, H. A., pH of Waters from Gas Condensate Wells Saturated with CO_2 at Various Pressures, Pet. Eng., **18,** 160 (1946) Nov.

Author's Reply to Discussions[1,2] of Paper Location and Selection of Anode Systems for Cathodic Protection[3]

By D. B. Good

MR. BRANNON inquires about the effect of breaking the 360 feet of 6-inch pipe buried horizontally, which was used for most of the illustrations in my paper, into two or more sections and placing them varying distances apart.

It has been our experience that the curves in Figure 6 showing "Resistance in Percent vs. Spacing Between Rods in Rod Diameters" can also be applied to horizontal groundbed spacings.

For instance, if two 180-foot sec-

tions are placed in line, with the ends about 60 feet apart, it will be found that the net resistance to earth is approximately one-half of a 180-foot section alone. The gain is of the following order:

Referring to Figure 3, the resistance is seen to be 0.27 ohm in a 1000 ohms per cubic centimeter soil for a 180-foot section, while for a 360-foot anode the resistance is 0.16 ohm. If the second 180-foot anode had been placed about 60 feet away from, and in line with the first 180-foot anode section, the resistance would have been about 0.14 ohm. In percentage we would have gained a 12 percent reduction in the anode resistance to earth. A study of actual installations bears out the above reasoning.

However, the 12 percent reduction in anode resistance to earth may have a much smaller weighted value when reflected into the total circuit resistance if the pipeline resistance to earth is appreciable.

The methods that can be used in determining the pipeline resistance to earth, or the anode resistance to earth are well covered in a booklet put out by the James G. Biddle Company described as "Ground Resistance Testing, Technical Bulletin 1285." For fifty cents this Bulletin may be obtained by writing the James G. Biddle Company, 1211-13 Arch Street, Philadelphia, Pa. Another good reference is the Bureau of Standards Technological Paper No. 108, "Ground Connections for Electrical Systems," by O. S. Peters, Assistant Physicist, June 20, 1918.

Mr. Mudd has vividly emphasized the variations that may be encountered in measuring soil resistivities at certain locations, and in this we can concur, as it is not always simple to determine the average soil resistivity. The curves of Figure 1 in his discussion show some marked variations of soil resistivity with depth, as determined by varying the electrode spacing. These curves bring to mind more than ever the importance of making soil resistivity readings, as with such data, the best compromise ground-bed location may be determined. Some of these curves show high soil resistivity at 5-foot depths, but markedly lower resistivities at 8-foot depths.

Where heavy castings are used, the vertical variation in soil resistivity might be more critical than where a horizontal pipe or rail is used, as the low resistance strata might be more easily followed with smaller diameter anodes.

The limitation of the Megger and four-bar method of determining soil resistivities is mainly one of the variations of the soil itself, and as such it is worthwhile to recognize and design, as Mr. Mudd points out, for the least favorable soil resistivity.

References

1. Brannon, R. A., Corrosion **3,** 632 (1947) Dec.
2. Mudd, O. C., Corrosion **3,** 633-635 (1947) Dec.
3. Good, D. B., Corrosion **3,** 539-548 (1947) Nov.

A Message from the Incoming President

F. L. LaQUE

THE organization of the National Association of Corrosion Engineers is such that the newly elected officers have for their guidance a Board of Directors of which most of the members have served previously. This assures that continuity of policy and practice which is so essential to the progress of the Association. This progress was considerable in the past year, which saw the membership practically doubled, the financial condition of the Association substantially improved, and many noteworthy technical accomplishments recorded. Upon this substantial foundation, and with the continued help of every member, your new officers are resolved to do their best to advance the Association even further and to consolidate the preeminent position it has achieved already amongst organizations concerned with corrosion.

Every effort will be made to increase the membership of the Association, and especially to attract active members from as many diverse fields as possible. In this way, the objectives of the Association in providing a means for applying experience in one field to the solution of problems in another may be accomplished most readily.

As the Association becomes larger, the danger of losing that freedom of discussion and real desire of the members to help each other, which has characterized the NACE from the start, must continually be kept in mind. The advantages inherent in a large, strong organization can be combined most effectively with the desirable close personal contacts of a small one through the activities of regional divisions and their local sections. It will, therefore, be our aim to continue our satisfactory rate of growth primarily through the attraction of new members to those local sections already in existence and through the organization of new local sections.

A strenuous effort will be made to secure additional sustaining associate and corporate memberships. This will provide funds for the effective technical activities of the Association and, at the same time, will enable each sustaining member to secure the full benefit from activities to which he has contributed only a small fraction of the cost.

To achieve our aims and continue the amazing progress already made by the young and vigorous organization, your officers are depending on the continued loyal and effective support of each and every member who is being counted on to be "active" in deed, as well as in name.

NACE News

The South East Regional Division of the National Association of Corrosion Engineers held their first meeting of 1948, March 3, in Birmingham, Ala. The program consisted of a one-day session, with business and field trips during the morning, a technical session in the afternoon, and dinner in the evening. During the technical session, the following papers were presented.

Eight General Types of Corrosion Attack, by Mars. G. Fontana, Professor of Metallurgical Research, The Ohio State University, Columbus, Ohio.

Corrosion in Power Industry, by H. W. Cauthen, Georgia Power Company, Atlanta, Georgia.

Methods of Accelerated Paint Testing, by W. M. Abernethy, Southern Research Institute, Birmingham, Ala.

Corrosion Prevention Practices at Atlanta Water Works, by A. T. Storey, Atlanta Water Department, Atlanta, Ga.

The papers were well received, and much enlightening discussion followed presentation of each.

The field trips were to American Cast Iron Pipe Company, Southern Research Institute and Tennessee Coal & Iron Co., and served a double purpose. They provided an informal atmosphere for getting acquainted and were most interesting. Each member was placed in a receptive frame of mind and gained valuable technical knowledge.

Dinner speakers were Tom L. Holcombe, Dearborn Chemical Company, Shreveport, La., and Chairman of the NACE Membership Control Committee, and Ivy M. Parker, Plantation Pipe Line Co., Bremen, Georgia, Editor of CORROSION.

During the business meeting, Charles B. Gamble, Regional Chairman, appointed H. C. Van Nouhuys Chairman of the Membership Committee, and Ivy M. Parker Chairman of the Program Committee. The next meeting of the South East group is tentatively scheduled in the Fall.

Houston Section of the South Central Region held a dinner meeting March 18 at the Houston Engineers Club. L. G. Vande Bogart, Research and Development Laboratories, The Crane Co., Chicago, Ill., held the interest of those present with a lecture on Corrosion as a Problem in Chemical Engineering.

F. L. LaQue, The International Nickel Co., Inc., Vice President of NACE and President-Elect of the Association for 1948-49, was the principal speaker during the March 11 meeting of the Shreveport Section.

Tulsa Section of the South Central Region met March 19 in that Oklahoma City. Following dinner, L. B. Nelson, Shell Pipe Line Corp., Cushing, Okla., read the paper, Coordination of Cathodic Protection Installations to Avoid Interference with Adjacent Structures.

North Texas Section of the South Central Region held a dinner meeting March 10 in Dallas. A technicolor film, Carbon Black Treasure, showing the manufacture of carbon anodes, was shown by H. H. Frash, the National Carbon Co., and was followed by a round-table discussion led by Mr. Frash.

A poll of members of the South Central Region to determine when and where the next meeting of the Region will be held resulted in Tulsa, Okla., being selected as the location and September as the approximate time. The exact date will be determined by the Chairman of the Arrangements Committee and his subcommittees.

Three grants to the University of Iowa for research in chemistry, totaling $10,500, have been accepted by the Finance Committee of the State Board of Education. They are: A gift of $7500 from John H. Witte & Sons, paint and varnish manufacturing firm of Burlington, Iowa; $1800 grant from the Nutrition Foundation, Inc., to Clarence P. Berg, professor of biochemistry, for amino acid research; and renewal for 1948-49 of the $1200 Allied Chemical & Dye Corp. fellowship in chemistry. The John H. Witte & Son gift to the chemistry department will be

Program Correction

The Central Office regrets that through a typographical error, the Dearborn Chemical Company, 310 S. Michigan Avenue, Chicago, Illinois, was omitted from the list of Exhibitors on Page 18 of the 1948 NACE Conference and Exhibition Program. The Dearborn Chemical Company has been one of the best supporters of NACE, as an exhibitor at Annual Meetings, an advertiser in Corrosion, and in time and effort contributed to Association work. We regret this error, and offer our apology to the Dearborn Chemical Company for this inadvertent omission.

Since the copy for the 1948 Conference and Exhibition program was released to the printers, the following companies have taken exhibition space:

Lukens Steel Company, Coatesville, Pa.

Shell Pipe Line Corp., Houston, Texas.

F. H. Maloney Co., Houston, Texas.

United Gas Pipe Line Co., Shreveport, La.

It has also been learned since the printing of the program that a paper prepared by Dr. Ulick R. Evans, 1948 recipient of the Willis Rodney Whitney Award in the Science of Corrosion, will be presented at 9:40 a.m. Thursday, April 8, during the Gas Industry Symposium. The title of the paper is Some European Research on Passivity.

used to support fundamental studies in the field of paint and varnish chemistry. According to Professor George Clockler, head of the department, the work will be directed by Professor Ralph Shriner, head of the division of organic chemistry.

The Annual Convention and the Industrial Finishing Exposition of the American Electroplaters' Society will be held concurrently in Atlantic City June 28 to July 1, 1948. The Society is observing its 35th anniversary this year. National Office of the Society is located in Jenkintown, Pa.

Waterways Experiment Station, an agency of the Mississippi River Commission, Corps of Engineers, Vicksburg, Mississippi, is in immediate need of qualified hydraulic, soil mechanics, mechanical, electrical and concrete research engineers to assist in the accomplishment of a greatly expanded research and investigational program.

Work in the hydraulics laboratory of the Experiment Station is devoted to practical problems in river and harbor and flood control engineering. Extensive experimentation is conducted on the design of hydraulic structures, such as spillways and stilling basins of major dams, and on works required for maintenance of depths of alignment of navigable channels.

The soil mechanics laboratory is concerned with routine testing to determine the strength and behavior of soils under different conditions which may be imposed and is engaged in original research and the development of soils-testing methods, equipment and techniques. A special branch of the soils mechanics laboratory is engaged in the design of flexible pavements for airports.

The concrete research laboratory is engaged in conducting all major research activities required by the Corps of Engineers pertaining to the basic improvement of concrete structures to be built by the Corps of Engineers.

A fourth technical division at the Experiment Station, the Research Center, serves as a technical information center for the Corps of Engineers and is responsible for reports and publications on research investigations.

Persons interested should submit Applications for Federal Employment (Form 57, which may be obtained from any local Post Office) to the Director, Waterways Experiment Station, Corps of Engineers, P. O. Box 631, Vicksburg, Mississippi.

W. R. G. Baker, General Electric Co., Schenectady, N. Y., representing the Radio Manufacturers Association, was elected vice-chairman of the Electrical Standards Committee of the American Standards Association at its February 4 meeting, in a move to give the electronics and radio industry greater representation in the national standardization work. Charles Rufus Harte, of the Connecticut Company, New Haven, Conn., representing the American Transit Association, was re-elected chairman of the committee. Sidney Withington, chief electrical engineer, New York, New Haven & Hartford Railroad Co., representing the Association of American Railroads, was re-elected vice-chairman representing the power section of the committee.

PERSONALS

J. **Bennett Hill** and **John M. Pearson** have been appointed directors of new divisions in the recently created research and development department of Sun Oil Co., Philadelphia. Mr. Hill, former manager of the development division of the manufacturing department, will head a chemical and engineering division, and Mr. Pearson, former director of physical research and development of the production department, will direct a physical division.

Johan Bjorksten, President of the Bjorksten Research Laboratories, Chicago, Ill., announced the addition of a patent department to his organization. The department has been established for service to clients, for collaboration with corporate patent departments, for counsel in chemical cases and for handling of chemical patent problems and negotiations. The department will be headed by Mr. Bjorksten, who is also registered to practice before the Patent Office. **S. Jackson,** L.L.B., has joined the department and **Foster York** has been retained as counsel.

John H. Curtiss, Chief of the National Applied Mathematics Laboratories of the National Bureau of Standards, was elected a fellow of the American Statistical Association by "unanimous vote of the Committee on Honors" for "his outstanding contribution to the profession" at the Association's annual meeting in New York, December 28-31, 1947.

Frank A. Jones, formerly associated with Terminal Railroad Company, St. Louis; Busch-Selzer Bros., Diesel Engine Company, St. Louis; and the Missouri Pacific Railroad, has been appointed Chief Engineer of Dearborn Chemical Company, with headquarters at the Company's general offices, 310 S. Michigan Avenue, Chicago, Ill. He will supervise all engineering activities, foam-meter equipment, and the development of new equipment. **E. A. Goodnow,** whom he succeeds, has relinquished his position due to ill health, but he will remain with the Company as Assistant Chief Engineer.

Election of **A. B. Kinzel** as President of Union Carbide & Carbon Research Laboratories, Inc., has been announced by William J. Priestley, Chairman of the Board. Mr. Kinzel graduated from Columbia University, A. B., in 1919, Massachusetts Institute of Technology in General Engineering, 1931, and the University of Nancy, France, D. Met. Ing., 1922, where he also received the degree of Doctor of Science.

William C. Shirley, Chief Metallurgist of the U. S. Reduction Company, was the principal speaker of the National Officer's Night of the Non-Ferrous Founders Society national meeting, held Feb. 9 in Chicago, Ill. Mr. Shirley's talk was "The History of an Aluminum Casting,"

which traced the melting, refining and alloying of the ingredients used to produce an aluminum casting alloy, and a discussion of the melting practices to be used by the foundry when the alloy was delivered to his shop. The talk consisted of a detailed account of the various types of aluminum used in the alloying of casting ingot, and a description of general methods of processing and preparing this type of material for the subsequent melting and alloying to ingot.

Several new appointments in the Technical Service and Development Department of Electro Metallurgical Company have been announced by S. M. Norwood, Vice President. **Russell Franks** was named Chief Metallurgist, with headquarters in Pittsburgh. The following men were named Division Managers of Service: **J. N. Ludwig, Jr.,** with headquarters in the Pittsburgh office; **R. J. Portman,** Chicago; and **F. W. Hanson,** New York. **W. B. McFerrin** was appointed District Manager of Service, with headquarters in Detroit.

M. A. Self has been elected Vice President in charge of sales and a Director of the Bee Chemical Company, at a joint meeting of the stockholders and the Board of Directors on February 2. Mr. Self has been Sales Manager of the company since 1947.

NEW PRODUCTS, MATERIALS AND SERVICES

A new form of zinc anode, designed to solve some of the common problems in electroplating, is now being manufactured by Wagner Brothers, Inc., of Detroit. Known by the copyrighted name, "Flat Top," because of its shape, the anode is so distinctive in appearance as to prevent accidental confusion with cadmium or tin ball anodes, thus avoiding mixing of plating solutions and the consequent loss of time and materials from shut-downs and dumping of plating tanks. The anode's smooth surface is free from gates and flash which frequently cause ball anodes to hang on the basket wires, and the effective plating area is from 20 percent to 25 percent greater than a ball of like diameter. The greater weight per anode reduces loading frequency. According to the manufacturers, the zinc is 99.99 percent pure. A four-page folder is available from Wagner Brothers, Inc., Dept. K, 438 Midland Ave., Detroit 3, Mich.

Said to remove all kinds of paint, varnish, lacquer, and enamel from both flat and curved sheet metal surfaces many times faster than conventional scrapers, a paint scraper of new design has been perfected by Carboloy Company, Inc., of Detroit, Michigan, and is being manufactured

and distributed nationally through retail hardware and paint stores by Red Devil Tools, Irvington, New Jersey.

Mirrofilm, a new low-priced clear plastic finish which is simply wiped on to protect most any surface, gives a brilliant, mirror-like finish and long-life protection to metal surfaces, painted wood surfaces and linoleum. It is applied with a clean, lint-free cloth and dries quickly. One coat is usually adequate. The coating is made by the Wype Corporation, 2214 Dolman St., St. Louis, makers of Wype, a brushless auto enamel. Mirrofilm has been tested thoroughly by United States Testing Company, Inc. The manufacturer claims that Mirrofilm is the only plastic film that has been approved as passing a **one year** weatherometer test without chipping, blistering, peeling, flaking, chalking, checking or scaling, and with perfect retention of gloss.

In announcing their redesigned and improved line of Porter Hand Power Cutters featuring 15 improvements, H. K. Porter, Inc., Somerville, Mass., stress a new degree of ease, strength, safety and performance in the cutting of bolts, rods, wire, cable, chain, bars and metal of all kinds. A folder describing the complete line and recommending the cutter that should be used for each kind of cutting job is available upon request.

The relative ease with which a metal can be machined to final shape is an important factor in its ultimate usefulness to industry, as it vitally affects production time and hence the cost of the product. Essentially 60 percent nickel, 30 percent silicon and 10 percent iron, Nisiloy was developed as an inoculating agent for gray iron, to afford structure control and thereby improve machinability, according to **Nickel Topics,** published by the International Nickel Company, Inc. Since the nickel-silicon contents are in the eutectoid proportion, the alloy has a much lower melting point than either nickel or silicon, and lower than that of cast iron. Because of this, and because of the relatively high specific gravity of Nisiloy, it penetrates and diffuses rapidly throughout the melt, avoiding any risk of floating and oxidizing into a surface scum or slag, and exerts a strong homogenizing influence upon the product. In addition to reduction in scrap losses through elimination of chilled edges, etc., Nisiloy has frequently enabled annealing to be dispensed with where such treatments were previously necessary to permit efficient machining. This not only effects a further saving of time and money, but avoids the impairment of strength which invariably results from annealing. Possible distortion of castings during the annealing operation is likewise avoided.

Research help for industrial customers, in choosing the right adhesives, sealers and coatings, is offered in a new brochure by Minnesota Mining and Manufacturing Co., St. Paul. Entitled, "3M Adhesives in Industry," the 28-page brochure contains 40 pictures, cites 18 case histories, and lists 26 of the more than

1000 formulae offered by the company's adhesives and coatings division in Detroit. Pictured are bonding operations such as plywood-to-metal and vinyl-sheeting-to-wood; sealing operations involving aircraft cabins, auto bodies, and boat decks; and protective and anti-corrosion coatings for metal. Included in the case histories are such industries as automotive, aviation, ship building, oil and refrigeration. Copies are available on request to the firm's offices at 901 Fauquier Avenue, St. Paul 6, Minn.

A magnesium anode may be the answer to the perennial household problem, the rusting hot water tank, according to research workers of The Dow Chemical Company, who have recently completed extensive tests in the application of cathodic protection for domestic water heaters. The anodes are made from Dow-supplied, small-diameter magnesium rods of special alloy and contain a core of steel wire to prevent breaking up of the anode at points where concentrated attack takes place. Moderately priced and easily installed, they may be used on any size or type of water heater. In existing heaters, the rod is adapted for convenient installation through the hot water outlet, without affecting hot water draw-off in any manner.

A rod when installed, extending the full length of the tank, is expected to last six years, but may need replacement at an earlier or later time depending upon the type of water used in the community, and just how aggressive the water is in attacking the metal. To afford best protection, anodes should be installed so as to extend within approximately three inches of the tank's bottom.

Several manufacturers are undertaking marketing of the rod, making anodes in varying sizes for supply to plumbers and heating dealers.

The fifth edition of the American Standard Specifications for Dry Cells and Batteries, approved by the American Standards Association on August 6, 1947, is now available as Circular C466 of the National Bureau of Standards. The new specification, to be known as American Standard C18-1947, covers the first-grade product of manufacturers and includes all the types of batteries commonly used by the public. Its technical requirements have also been incorporated into a revision of Federal Specification W-B-101. The circular may be obtained at a cost of 10 cents from the Superintendent of Documents, Washington 25, D.C., or from the American Standards Association, 70 East 45th Street, New York, N. Y.

Clean, bright surfaces on Lukens Steel Company's alloy and alloy-clad steel products through thorough removal of metallic oxide films is expected with the recent installation of a new sodium hydride descaling unit at the company's mill in Coatesville, Pa. The equipment will be used on all metals not affected by molten caustic or by heating at 700° F. Savings in metal, more uniformly descaled surfaces, and shorter descaling time are claimed as the principal advantages offered by the new process over blast cleaning.

Corrosion Abstracts

Unusual Cause and Effect of Corrosion. A. H. STUART. Pet., **10,** 26+ (1947) Feb.

Describes an unusual case. The packing of a centrifugal water pump developed a leak. The graphite impregnated asbestos packing was found to be deteriorated and to contain ferric hydroxide flakes. These were traced to an iron content of over 6% in the natural graphite used. Also examined a micaceous hematite which had been submitted as a graphite substitute, and it had had no lubricating properties.—BLR.

Rate of Corrosion of Lead by Hydrocarbon Solutions of Organic Acids. D. TURNBULL & D. R. FREY, J. Phys. Coll. Chem., **51,** 681-704 (1947) May.

The effect of acid structure and concentration on the corrosion rate of lead in hydrocarbon solutions was studied using an air at atmospheric pressure as the fixed oxidizing agent and under conditions which serve to reduce the depth of the diffusion layer surrounding the test specimen. The acids used were acetic, butyric, phenol heptylic, capric naphthenic, lauric palmitic oleic and stearic. Benzene and xylene were used as solvents. A number of general facts were noted including (1) for organic acid solutions of 0.01 molar or less in the temperature range from 70-80° C., the direct corrosion products are basic lead salts; (2) the corrosion rate is independent of oxygen pressure in excess of that supplied by air; and (3) the acids fall into two groups exhibiting different behaviors. Theories of this type of corrosion are discussed in detail.

Mechanism of Protective Action of Alloying Elements During the Sulfide Corrosion of Iron. (In Russian.) P. V. GELD & O. A. ESSIN, J. Applied Chem. (USSR), **19,** No. 9, 861-868 (1946).

A new interpretation of the mechanism of the protective action of alloying elements vs. sulfur corrosion is proposed. In this way, the protective action of chromium and aluminum and the absence of such action in the case of nickel and manganese are explained. 17 references. —BLR.

Concentration of Sulfuric Acid Under Vacuum. J. F. BURKE & E. MANTIUS, National Lead Co. Chem. Eng. Prog., **43,** No. 5, 237-246 (1947) May.

Reasons for attempting the high concentration of H_2SO_4 under vacuum and the development of the

Simonson-Mantius process are discussed. The types of concentrators handled in each and proper materials are covered. In heating elements of concentrators, the best materials from the point of view of corrosion and adaptability to the process are St. Joe chemical lead and Karbate for low and medium concentrations, and 14% silicon iron and Hastelloy for high concentrations. Hastelloy D has been used with acid as low as 40% acidity, but is best suited for concentrations between 65% and 95%. Tantalum bayonet heaters are also used. Concentrator bodies for high concentrations are of steel lined with chemical lead. Hot acid is handled in Hastelloy D in carbon or lead-lined steel pipes. Equipment is shown in detail.—INCO.

Corrosion of Concrete Caused by Sulphur-Oxidizing Bacteria. C. B. TAYLOR & G. H. HUTCHINSON, J. Soc. of Chem. Ind., **66**, 54-57 (1947) Feb.

Serious corrosion of large concrete cooling towers was found to be associated with the activities of sulfur-oxidizing bacteria which were found to be present in large numbers in the circulating waters and the wet corroded material.—BLR.

Corrosion Report. ASTM Advisory Committee on Corrosion. W. H. FINKELDEY, Chrm. (ASTM Phila.) gratis (TA-467, A-51) 14 pp. (1947) May 23.

This report is an account of the corrosion work undertaken by various A. S. T. M. Committees and summarizes briefly the principal activities that each has followed. The committees include A-5 on corrosion of iron and steel, A-10 on iron-chromium, iron-chromium-nickel, and related alloys, B-3 on corrosion of non-ferrous metals and alloys, B-4 on electrical heating, resistance, and related alloys, B-6 on die cast metals and alloys, B-7 on light-metals and alloys, cast and wrought, B-8 on electro-deposited metallic coatings, D-1 on paint, varnish, lacquer and related products, and D-19 on water for industrial uses.

Surface Attack on Light Metals. H. A. J. STELLJES, Translation from Aluminum, **19**, 291-298 (1937).

Deals with such matters as surface attack from abrasion, from condensation and from pitting. Written for rather "popular" consumption.—BNF.

Rate of Oxidation of an Austenitic Iron-Chromium-Nickel Alloy. I. I. KORNILOV & A. I. SPIKELMAN, Comptes Rendus (Doklady) Acad. Sciences URSS, **54**, No. 6, 511-514 (1946) Nov. 30.

Scaling tests of 750 hours duration were carried out at 1100° and 1200° C. on a steel with 28% chromium and 27% nickel. Analysis of the descaled specimens showed that carbon, silicon and at 1100° carbon, chromium were preferentially oxidized, while the relative nickel content increased.—BNF.

Corrosion of Some Magnesium-Base Alloys (High and Normal Purity) in Contact with Other Metals. F. A. FOX & J. K. DAVIES, J Inst. Met., **73**, No. 9, 553-566 (1947) May.

A study has been made of the corrosion of magnesium-base alloys (mainly those containing 5% alumi-

num) of normal and high purity, immersed in 3% sodium chloride solution saturated with magnesium hydroxide, while in electrical contact with other metals. The work shows that, in general, the cast magnesium alloy containing 5% aluminum behaves anodically to other metals when immersed in the corroding solution, exceptions being cast aluminum of high purity and some Elektron alloys.—BNF.

Corrosion of Filters in Sugar Refineries. Part I — Investigations Using Plant Liquors. Part II—Investigations on Prepared Liquors. H. INGLESENT & J. A. STORROW, Ind. Chem. **23,** Nos. 268 & 269, 291-297, 373-379 (1947) May, June.

Investigations include reference to failures arising from use of dissimilar metals on the plant. Mention is made of copper, brass, Monel, phosphor bronze, stainless steel.—BNF.

Corrosion of Metals. Part VII — Zinc and Its Alloys. Sheet Met. Ind., April, 1947, **24,** No. 240, 801-806. In progress.

Present installment, the first on zinc and its alloys, surveys corrosion of zinc pressure-diecasting alloys (particularly effect of impurities and small alloying additions) and of some German wrought zinc alloys. Some figures on unalloyed zinc are included.—BNF.

An Electron Diffraction Study of Oxide Films Formed on High Temperature Oxidation Resistant Alloys. J. W. HICKMAN & E. A. GULBRANSEN, Westinghouse Research Laboratories, East Pittsburgh, Pa., Electrochem. Soc. Preprint 91-32, 467-483 (1947).

The electron diffraction reflection technic is used to study the structures of the oxides which form on aluminum-chrome-6, Worthite, stainless steels 301, 446 and alloy S-588 in the temperature range 300° to 900° C. These materials are steels high in chromium, or chromium plus nickel, or chromium plus aluminum, etc. Photographs of the oxides are taken at the temperatures of formation in order to eliminate the possibility of chemical and physical changes which may occur upon cooling. The structures found are plotted on existence diagrams as functions of time and temperature. Attempts are made to correlate the structures obtained with thermodynamic data reported by other workers. The oxides on all of the alloys over the complete time-temperature range consist of Cr_2O_3 or a spinel type structure which may be solid solution of two or more oxides. Spectrographic analyses indicates that nickel is absent in the outer oxide layer. There does not appear to be any unique mechanism for the oxidation of ferritic and austenitic stainless steels.

Mechanical Properties and Corrosion Resistance of Magnesium, Manganese Alloys Containing Nickel, Copper and Silver. C. J. BUSHROD & H. T. HALL, Magnesium Rev. and Abs., **6,** 52-56, (1946); Chem. Abs., **41,** No. 6, 1592 (1947) March 20.

A magnesium-base alloy containing 2 percent manganese was converted into 3 different ternary alloys containing 4 percent nickel, 3 percent copper and 7 percent silver, re-

spectively. When tested for corrosion resistance in 3 percent sodium-chlorine solution for 7 hours, the nickel alloy showed rapid attack, corroding about 1000 times as fast at Elektron A-8. Microstructure of the alloy containing silver indicates primary manganese particles and magnesium 3 silver phase, while the copper alloy shows primary manganese particles and the —Mg_2Cu phase. Tensile determination show that these alloys are of no interest in the as-cast condition either for room-temperature or high-temperature use. Corrosion tests in a 3 percent NaCl solution for 24 hours showed for the Cu alloy about 240 times and for the Ag alloy about 8.4 times as much loss as obtained with Elektron A-8. 2 references.—INCO.

Contact Corrosion of Aluminum Alloys. K. MATTHAES & W. SCHULTZ, Translation from Luftfahrforschung, **15,** 54-59 (1938).

An investigation of the corrosion in synthetic sea-water and in 3 percent sodium chloride of aluminum and aluminum alloys in contact with various non-ferrous and ferrous metals and alloys. Includes measurement of electric potential differences arising.—BNF.

New Theory for Corrosion of Carbon Steel. WILLIAM C. UHL, Petro. Processing, **2,** 405-408 (1947) June.

Detailed and critical discussion of new theory that the structure of the carbide crystals in steels is the important factor controlling corrosion. Metal surface areas rich in lamellar pearlite are said to be more resistant than areas in which the carbide structure is in spheroidized form.—BLR.

Metals in Service. P. M. HESS, Safe Harbor Water Power Corp., Metals Rev., **20,** No. 1, 37 (1947) Jan.

Discussion of the problem of corrosion and pitting resulting from barnacles and cavitation. In cavitation of turbine blades, the solution lies in chipping out the affected areas and welding in a layer of 18-8 stainless steel.—INCO.

Use of Glass Wool as Thermal Insulation in Light-Alloy Apparatus. (In French.) JEAN HERENGUEL, Revue de l'Aluminium, **24,** 10-11 (1947) Jan.

Corrosion of a double-walled electric boiler made of an aluminum-magnesium alloy having glass-wool insulation between the walls, was investigated. It was found that alkalinity of the insulating material and the presence of water should be avoided in order to eliminate corrosion at temperatures above 100° C. —BLR.

New Research on the High-Temperature Oxidation of Iron by Micrographic Methods. (In French.) J. BENARD & O. COQUELLE, Revue de Metallurgie, **43,** 113-124 (1947) Mar.-Apr.

Thorough X-ray investigation of a large number of test specimens permitted establishment of the dependence of iron oxide growth and structure on the temperature and nature of the alloying elements. Diagrams and photomicrographs illustrate the indicated relationship. 10 references. —BLR.

Progress in Corrosion and Heat Resisting Steels. L. SANDERSON, Eng. & Boiler House Rev., **61,** 199-200

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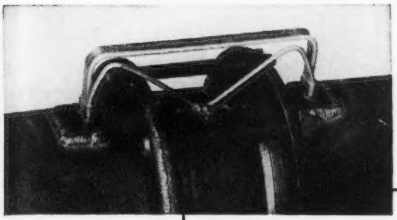

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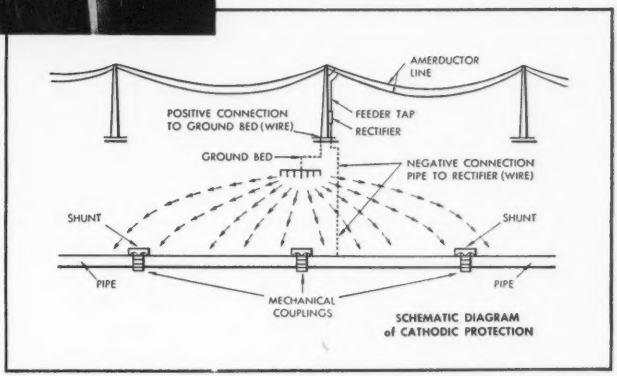

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U·S·S American Pipe Coupling Shunts

(1946) Dec.; Corros. & Mat. Prot., **4,** No. 3, 28 (1947) May-June.

Reviews new steels developed for resistance to heat and corrosion and developments in processes, investigations into corrosion resistance, properties, and behavior, and other aspects of stainless and heat-resisting steels.—INCO.

Chemical Activity of Metal Surfaces as Influenced by Various Conditions of the Metal. J. A. HEDVALL, Harald Nordenson, 165-176 (1946) (In English); Chem. Abs., **41,** No. 7, 1980 (1947) April 10.

Examples are presented to illustrate the principle that in transitional states solid substances attain a relative max. of activity. In Curie transitions of metallic and nonmetallic ferromagnetic substances the catalytic effect increases. The tarnishing velocity of metals is accelerated by supersonic vibrations.—INCO.

Investigation of Stress Corrosion, Parts I and II. B. C. MADDEN, Am. Met. Market, **54,** No. 104, 1, 8 (1947) May 29.

The resistance of aircraft structural materials to spontaneous cracking while exposed to the atmosphere under stress can be estimated more quickly on the basis of two new criteria developed by the U. S. Army Air Forces, according to a research report entitled "Investigation of Stress Corrosion" and recently published in two parts. Part I is an early progress report dealing mainly with the methods used to expose and stress three types of test specimens. It contains test data, as well as 34 photomicrographs showing stress corrosion cracks and the effect of corrosive exposure on various light metal alloys. Part II describes the development and application of new standards for measuring stress corrosion resistance, and lists 23 aluminum alloys and 12 magnesium alloys in order of decreasing resistance to corrosion. One of the new stress corrosion resistance criteria involves strength measurements after accelerated exposure and stress, and the other, elongation measurements under similar conditions. Strength sensitivity is considered the better of the two, but elongation sensitivity may be used to check strength sensitivity findings. Stress corrosion resistance was investigated to obtain improved test methods. The test considered most satisfactory for magnesium alloys was intermittent immersion of static tensile specimens in distilled water, approximating the corrosive effect of vapour condensation either at high altitudes or on the ground, as well as of rain and fog. In the case of aluminum alloys intermittent immersion of static tensile specimens in a 3½ percent sodium chloride solution was found to approximate the corrosive effect of sea spray.—ALL.

Submerged Melt Welding of Corrosion-Resistant Metals. R. J. ANDERSON & H. J. ROBERTS, Can. Metals & Metall. Ind., **10,** No. 2, 18-19 (1947) Feb.

Discussion of the problems encountered and the corrective measures necessary to obtain satisfactory welds of the corrosion-resistant metals. It includes the welding of some heat-resistant metals by the submerged melt welding process.

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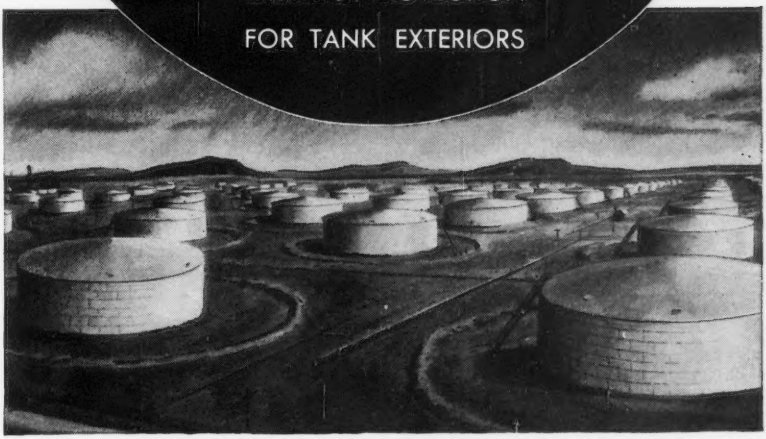

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Kinetics of Oxide Film Formation on Metals and Alloys. E. A. GULBRANSEN, Electrochem. Soc., Preprint 91-29 (1947) April.

The kinetics of the oxidation process is broken down into eleven fundamental factors. These are: (1) time, (2) temperature, (3) pressure, (4) surface preparation and passivation treatments, (5) gas in the metal lattice, (6) surface area, (7) crystal orientation, (8) gas flow, (9) cycle oxidation, (10) vacuum effect, and (11) stability of the oxide film. Rate experiments on the metals aluminum, magnesium, tungsten, molybdenum and iron and the alloy 18/8 stainless steel are used to illustrate the effect of the various variables. The metals and alloys are found to follow the parabolic rate law over a certain time and temperature range. Deviations are found for higher temperatures. These deviations are found to be independent of film thickness, surface preparation and pressure. The transition rate theory of gas metal reactions is applied to compare the oxidation behavior of each metal. The energies of activation vary from 22,600 calories/mol for iron to 45,650 calories/mol for tungsten. The entropies of activation vary from —28.7 for 18/8 stainless steel to 11.2 for tungsten. The entropy of activation is a measure of the frequency factor or the probability of reaction for a definite energy of activation. The oxidation rate is interpreted from this point

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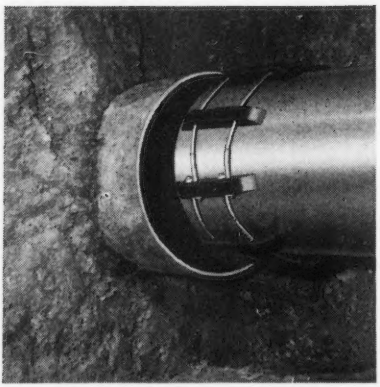

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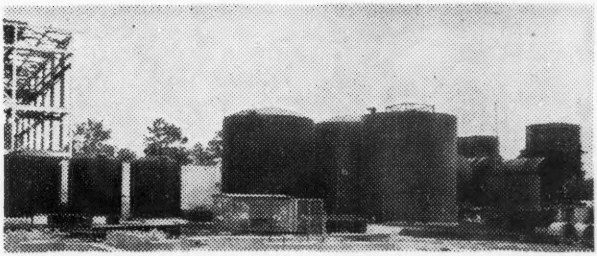

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of view. The influence of the other variables are presented and briefly discussed.—ALL.

Aluminum Solder. L. R. VOIGT, Power, **91,** No. 7, 178-180 (1947) July.

Corrosion-resistant bonding material Alsoco permits soldering aluminum to aluminum without flux or flux substitute. Tests revealed material resisted shearing after a 250-hr. salt-spray corrosion test states the maker, with three grades showing 3%, 8.6%, and 4.6% loss in strength. Further information resulting from these tests showed; 1) an increase in resistance of an aluminum wire soldered to a copper lug from 20 microhms to 28 microhms after 250-hr. salt-spray; 2) no failure of the solder itself in vibration tests to failure of a ¼-in. and a ⅜-in. standard aluminum wire soldered to a copper lug.—ACO.

Contact Corrosion Problems in the Metal Industry. E. F. PELLOWE & F. F. POLLAK, Metallurgia (Eng.), **36,** No. 212, 67-70 (1947) June.

The contact corrosion of cast aluminum to steel, galvanized steel, brass, pure aluminum and stainless steel has been studied. The method adopted was to make accurately weighed discs of the various materials; these were placed in contact and the pairs of discs were submitted to a period of immersion in salt solution for several weeks and the samples were then cleaned and reweighed; control sets of similar metals were included to asses the increase of attack due to dissimilarity; the systems were studied in the painted and unpainted condition. The results: (1) For metal to metal contact are of the same order as those obtained by the American So-

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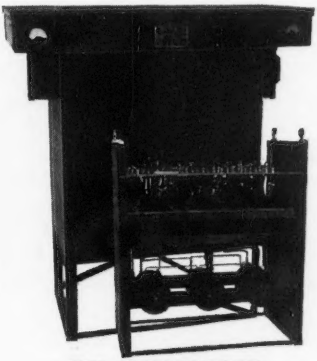

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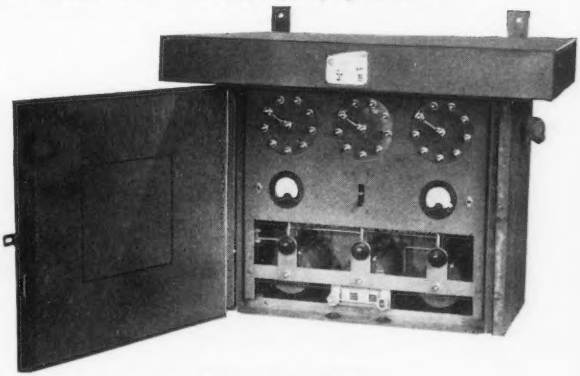

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ciety for Testing Materials, (2) form an addition to our knowledge in that they deal with commercial alloys rather than with pure metals, (3) indicate that as far as these painted systems are concerned, contact corrosion is negligible, (4) fill a gap in the A. S. T. M. figures since the latter omit the aluminum/iron system. (Author's summary.)—ALL.

Nature of Etching Pits in Quenched Copper-Aluminum Light Alloys. H. KAWAI, J. Chem. Soc. of Japan (Japan) **63,** 1114-1130, (1942).

The test piece of copper-aluminum alloy (copper = 3.85) was annealed 2 hours at 520° C. (968° F.), quenched in ice water, and etched with 25% HNO_3 and then with Keller's reagent (0.5 grams sodium-fluoride, 2 cc. concentrated hydrochloric acid, and 1 cc. concentrated nitric acid are dissolved in water, and the solution is made up to 100 cc.). Seven photomicrographs are given. The test piece was rolled, annealed 15 hours at 500° C. (932° F.), quenched in ice water, and subjected to X-ray examination by the Laue method. The forms of the etching pits appearing in the surfaces of various single crystals are analyzed. The work of M. L. V. Gayler is criticized. (Chem. Abs. (USA) **41,** No. 10 3032, (1947) 20th May.—ALL.

High Temperature Corrosion of Metals Under Alternate Carburization and Oxidation. H. K. IHRIG, Globe Steel Tubes Co., Electrochem.

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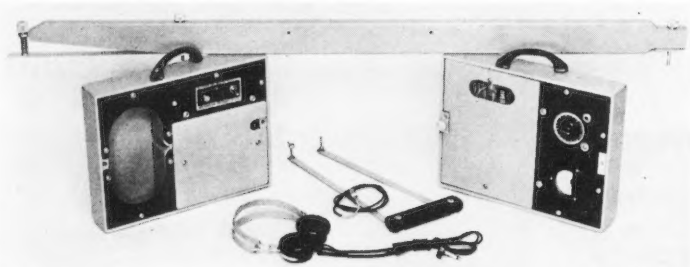

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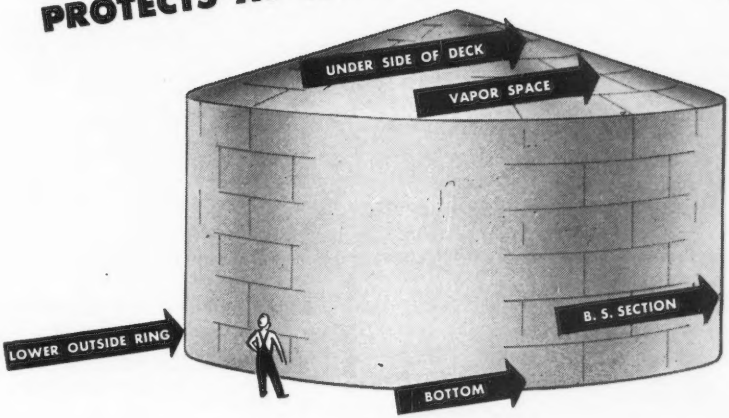

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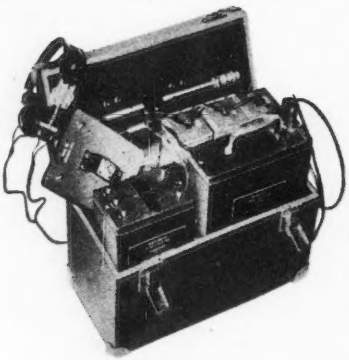
Soc. Preprint 91-3, Adv. copy, 333-344 (1946).

The corrosion of metals under alternating oxidation and carburization cycles at high temperatures encountered in catalytic processes offers new problems in the use of metals in the design of large scale equipment. The metals must withstand oxidation, reduction and carburizing. In addition, they must not poison the catalyst. A laboratory, and extensive pilot and large commercial plant tests are described. From the evidence presented, it is believed that the high chrome steels such as 26 percent chromium alloy are the best for this service. The protective action of small amounts of sulfur in the feed stock is also described.—INCO.

Anodic Behavior of Sacrificial Metals in Specific Environments. K. M. WIGHT & R. F. HADLEY, Amer. Gas Assoc., Interim Report, 30 pp. (1947).

Experiments were designed to test the suitability of various types of chemical backfills for the sacrificial anodes which are as follows: zinc, magnesium with 6 aluminum and 3 zinc, aluminum with 5 zinc, and aluminum with 10 zinc. Purpose was to perform experiments in the laboratory in order to select chemical environments suitable for investigation under field conditions. It involved a study of anodic reactions and anodic polarization. Photographs show instruments used and views of the corrosion cells in the tanks, and graphs show the performance of the different cells. 15 references.—INCO.



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Contribution to the Question of the Stress-Corrosion Properties of Aluminum-Magnesium-Zinc Alloys. W. BERGMANN & W. GUERTLER, Korrosion u. Metallschutz, **19,** No. 6, 160-165 (1943); J. Inst. of Metals & Metall. Abs., **14,** 103 (1947) March.

A study was made of the corrosion-resistance of the aluminum-magnesium-zinc forging alloy G.54 after small additions of silicon, copper, thorium, vanadium, manganese, titanium, and iron, after air-cooling from the solution temperature and after solution treatment and heat-treatment for 14 days at 60°-70° C. The tests were carried out in air and by stirring-corrosion, alternate-dipping, and spray tests in tap water, artificial sea water, and salt solution for periods up to 14 days.—INCO.

Alloys for Heat and Corrosion-Resistant Castings. Am. Machinist Ref. Book Sheet. Am. Machinist, **91,** No. 2, 215 (1947) Jan. 16.

Revised designations for general composition of alloys for heat and corrosion-resistant castings issued by the Alloy Casting Institute, are tabulated. List comprises 46 designations. Complete chemical compositions are not given with these designations because the exact chemistry of the alloy supplied depends upon the application. Composition ranges with the designations show nickel, chromium and carbon content as well as the normal ranges of special alloy additions such as molybdenum, cobalt and selenium. Carbon content is not shown. Significance of symbols is explained.—INCO.

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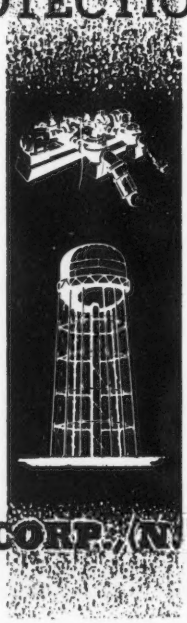

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Oxidation of Metals. W. E. CAMPBELL & U. B. THOMAS, Electrochem. Soc., Preprint 91-24, 16 pp. (1947).

A simple method is described for measuring oxidation rates at elevated temperatures. Oxidation rate of copper is measured in pure oxygen at five temperatures from 100° to 256° C. Annealed copper is shown to oxidize more rapidly than unannealed copper at 169° C., an effect which is believed to be due to an increase in specific surface due to recrystalliization in annealing. The oxidation-rate curves for a large number of copper alloys, nickel, and stainless steel are presented.—BLR.

Corrosion and Oxidation Experiments in High Pressure and High Temperature Steam Service. PAUL M. BRISTER & J. B. ROMER, Electrochem. Soc., Preprint 91-17, 23 pp. (1947).

Deals with the corrosion experienced with metals used for steam generating tubes and superheater tubes for high pressure boilers. Methods of relief and interpretation of the causes of corrosion of steam generating tubes are presented.—BLR.

Cast Alloys Stabilized with Columbium or Titanium. E. A. SCHOEFER, Alloy Casting Bull., 1-7 (1947) May.

Summarizes information on the influence on corrosion resistance of columbium and titanium additions to CF - type chromium - nickel alloys, given in report submitted to A.C.I. by Battelle Memorial Institute.—BLR.

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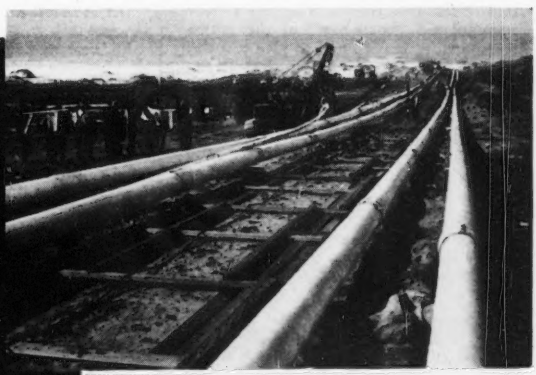

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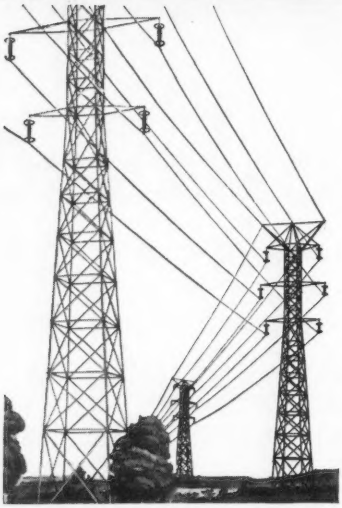

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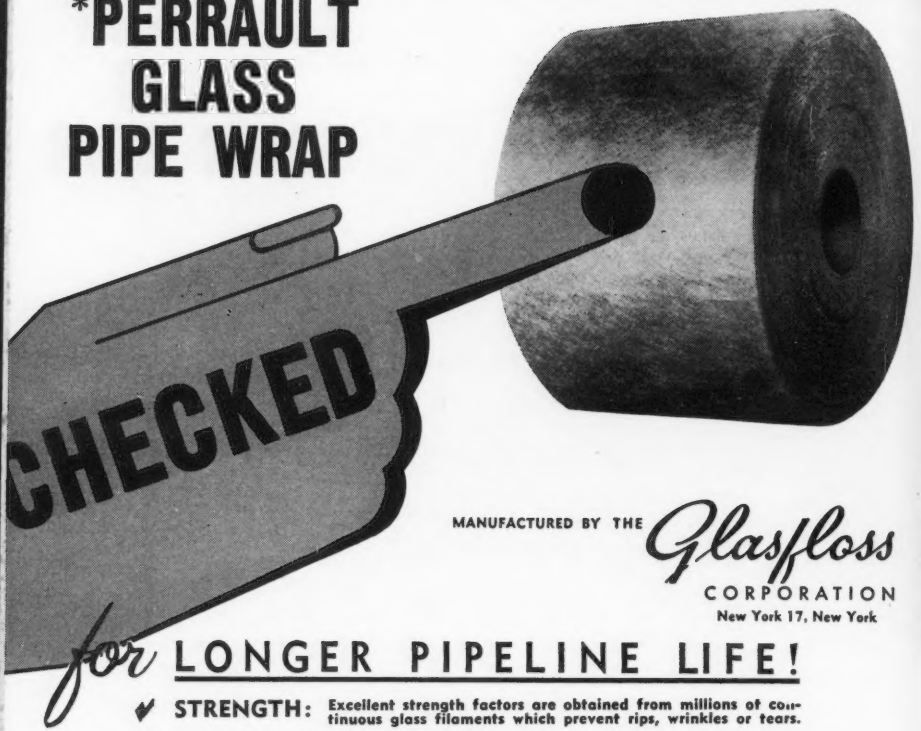

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